

T H E

	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT		SYMBOL
<i>Aluminum</i>	Al	13	26.97	<i>Holmium</i>	Ho
<i>Americium</i>	Am	95		<i>Hydrogen</i>	H
<i>Antimony</i>	Sb	51	121.76	<i>Indium</i>	In
<i>Argon</i>	A	18	39.944	<i>Iodine</i>	I
<i>Arsenic</i>	As	33	74.91	<i>Iridium</i>	Ir
<i>Astatine</i>	At	85		<i>Iron</i>	Fe
<i>Barium</i>	Ba	56	137.36	<i>Krypton</i>	Kr
<i>Beryllium</i>	Be	4	9.02	<i>Lanthanum</i>	La
<i>Bismuth</i>	Bi	83	209.00	<i>Lead</i>	Pb
<i>Boron</i>	B	5	10.82	<i>Lithium</i>	Li
<i>Bromine</i>	Br	35	79.916	<i>Lutetium</i>	Lu
<i>Cadmium</i>	Cd	48	112.41	<i>Magnesium</i>	Mg
<i>Calcium</i>	Ca	20	40.08	<i>Manganese</i>	Mn
<i>Carbon</i>	C	6	12.010	<i>Mercury</i>	Hg
<i>Cerium</i>	Ce	58	140.13	<i>Molybdenum</i>	Mo
<i>Cesium</i>	Cs	55	132.91	<i>Neodymium</i>	Nd
<i>Chlorine</i>	Cl	17	35.457	<i>Neon</i>	Ne
<i>Chromium</i>	Cr	24	52.01	<i>Neptunium</i>	Np
<i>Cobalt</i>	Co	27	58.94	<i>Nickel</i>	Ni
<i>Copper</i>	Cu	29	63.54	<i>Niobium</i>	Nb
<i>Curium</i>	Cm	96		<i>Nitrogen</i>	N
<i>Dyprosium</i>	Dy	66	162.46	<i>Osmium</i>	Os
<i>Erbium</i>	Er	68	167.2	<i>Oxygen</i>	O
<i>Europium</i>	Eu	63	152.0	<i>Palladium</i>	Pd
<i>Fluorine</i>	F	9	19.00	<i>Phosphorus</i>	P
<i>Francium</i>	Fr	87		<i>Platinum</i>	Pt
<i>Gadolinium</i>	Gd	64	156.9	<i>Plutonium</i>	Pu
<i>Gallium</i>	Ga	31	69.72	<i>Potassium</i>	K
<i>Germanium</i>	Ge	32	72.60	<i>Praseodymium</i>	Pr
<i>Gold</i>	Au	79	197.2	<i>Promethium</i>	Pm
<i>Hafnium</i>	Hf	72	178.6	<i>Protactinium</i>	Pa
<i>Helium</i>	He	2	4.003	<i>Radium</i>	Ra

E L E M E N T S

ATOMIC NUMBER	ATOMIC WEIGHT		SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT
67	164.94	<i>Radon</i>	Rn	86	222
1	1.0080	<i>Rhenium</i>	Re	75	186.2
49	114.76	<i>Rhodium</i>	Rh	45	102.9
53	126.92	<i>Rubidium</i>	Rb	37	85.4
77	193.1	<i>Ruthenium</i>	Ru	44	101.1
26	55.85	<i>Samarium</i>	Sm	62	150.4
36	83.7	<i>Scandium</i>	Sc	21	45.1
57	138.92	<i>Selenium</i>	Se	34	78.9
82	207.21	<i>Silicon</i>	Si	14	28.0
3	6.940	<i>Silver</i>	Ag	47	107.8
71	174.99	<i>Sodium</i>	Na	11	22.9
12	24.32	<i>Strontium</i>	Sr	38	87.6
25	54.93	<i>Sulfur</i>	S	16	32.0
80	200.61	<i>Tantalum</i>	Ta	73	180.8
42	95.95	<i>Technetium</i>	Tc	43	
60	144.27	<i>Tellurium</i>	Te	52	127.6
10	20.183	<i>Terbium</i>	Tb	65	159.2
93		<i>Thallium</i>	Tl	81	204.3
28	58.69	<i>Thorium</i>	Th	90	232.1
41	92.91	<i>Thulium</i>	Tm	69	169.4
7	14.008	<i>Tin</i>	Sn	50	118.7
76	190.2	<i>Titanium</i>	Ti	22	47.9
8	16.0000	<i>Tungsten (Wolfram)</i>	W	74	183.9
46	106.7	<i>Uranium</i>	U	92	238.0
15	30.98	<i>Vanadium</i>	V	23	50.9
78	195.23	<i>Wolfram (Tungsten)</i>	W	74	183.9
94		<i>Xenon</i>	Xe	54	131.3
19	39.096	<i>Ytterbium</i>	Yb	70	173.0
59	140.92	<i>Yttrium</i>	Y	39	88.9
61		<i>Zinc</i>	Zn	30	65.3
91	231	<i>Zirconium</i>	Zr	40	91.2
88	226.05				

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INTRODUCTORY CHEMISTRY

*For Students of Home Economics
and Applied Biological Sciences • By*
LILLIAN HOAGLAND MEYER

Western Michigan College of Education

NEW YORK

THE MACMILLAN COMPANY

540

Chemistry

M576

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Preface

T*HIS BOOK* is the result of a fortunate series of opportunities. First, there was the opportunity for the author, with training and teaching experience in chemistry, to teach nutrition in a department of home economics and get the viewpoint of the home economist. Along with this came the opportunity to know many home economists and to learn a little of their problems on the job. Finally there came the opportunity to teach chemistry to home economics students and to try to develop with the help of many associates a course of study which would most effectively meet the needs of these students. The development still continues. But meanwhile, there was the urgent need for a textbook geared to the requirements of the future home economist and perhaps to the needs of many students in allied applied biological fields where the subject matter requirements are substantially the same.

The students to whom the book is addressed are freshmen who will take one year and very little more of chemistry. Some students approach chemistry with such a feeling of apprehension at its difficulty that they are unable to grasp even simple relationships. Yet if this fear can be removed, they are able to make satisfactory progress and to find that chemistry is an indispensable and useful tool in their chosen fields. An attempt has been made to present chemistry in simple terms, an informal manner, and short sentences. Readily understandable applications have been used to illustrate principles.

A knowledge of organic chemistry is essential to the study of foods, nutrition, and textiles. In nutrition some knowledge of the chemistry of the body is important. The problem of incorporating organic chemistry and some elementary biochemistry in the first year course is difficult. Before profitably approaching

the study of organic chemistry a student must have basic knowledge of the sphere of chemistry, of atoms and molecules, of chemical compounds, and of simple chemical reactions and their characteristics. The first part of the book contains material usually covered in an introductory course in chemistry. It has of course, been necessary to omit some parts and to abbreviate others. For example, methods of determining atomic weights have been omitted and chemical equilibrium has for the most part been intertwined with other material. However, since chemistry is a science and since an appreciation of the scientific method should grow out of any course in a science, proof of many ideas and discussion of the development of theories has been included. Likewise since chemistry is, in many of its aspects, an exact science, mathematical relationships and problems have been included. The second part of the book includes a long chapter on organic chemistry and short chapters on elementary biochemistry and textile chemistry.

The book contains more material than can be successfully digested in a one year course. At least this is the experience of the author. In her courses she omits the chapters on Nonmetals, Metals, and Atmosphere, but she has included them in the book since some teachers feel that this material must be covered and that it is more profitable to omit other sections. The author devotes almost the entire second semester to the study of organic chemistry, biochemistry, and textile chemistry. Some chapters are included to stimulate student interest. An example is the chapter on Glass and Pottery. For psychological effect the chapter on Leavening Agents is placed after the material on Solutions, Ionization, Colloidal Dispersions, and Quantitative Solutions. Its applications to a familiar field are readily understood and the author believes that student interest is thereby stimulated.

The author is particularly grateful to the many friends who through suggestions and criticisms have helped with the development of this book. Among these are Miss Sophia Reed, Miss Rachel Acree, Miss Mary Moore, Miss Betty Taylor, Dr. Gerald Osborn, and Dr. Alfred Nadelman of Western Michigan College of Education; Mrs. Frances Sanderson, Mrs. Dorothy Hill, Mrs. Katherine Burgum, and Dr. Helen Miner of Wayne University; Dr. Vivian Roberts of Ohio University; Dr. Janice Smith of the

University of Illinois; Dr. Margaret Fincke of Oregon State College; and Dr. Margaret Ohlson of Michigan State College. The author thanks Mr. Frank Householder for reading part of the manuscript.

In writing this book, the performance may have fallen short of the goal. Criticisms and suggestions for its improvement will always be gratefully received.

Lillian Hoagland Meyer

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INTRODUCTORY CHEMISTRY

Chemistry

AND THE STORY OF ITS DEVELOPMENT

INTRODUCTION

Unless you have grown up in a very isolated part of the world, you have heard the word *chemistry* and been aware of the fact that this science markedly affects your life. You know of new dyes and fabrics, new drugs, new fertilizers, new building materials — a great host of things produced by applied chemistry.

You will soon learn that chemistry will be a useful tool to you in the study of your vocation. In food preparation, chemical principles will often help you understand a cookery procedure. In nutrition a knowledge of biochemistry is essential to complete understanding of the effect of food on the body. In textiles, chemistry plays an ever increasingly important role in development and improvement of fabrics and dyes.

What Is Chemistry?

Chemistry is the study of the composition of the material world, of the forces which bring about change in composition, and of the results of these changes. As man has observed and experienced his environment down through the ages, he has at last found methods for partially understanding and partially controlling it.

These methods constitute the *scientific method*. Man has been only partially successful in his understanding and control because the use of the scientific method is relatively new in the history of man's development. You can immediately think of many factors in your environment which cannot be controlled — weather, aging, life and death, and many more. Perhaps man will never completely understand his environment and completely control

it. But when every year sees an increase in knowledge and a greater possibility of control of sections of our environment, one feels confident that the development of insight is just beginning.

What Is the Scientific Method?

Those who are called scientists carry out their studies of our environment by isolating minute bits and studying them meticulously. If you ride on a speeding train through a state which you have never visited before, you get a very general and hazy idea of the character of the place. But if you get off the train and spend a year in one small village, you understand more fully the character of the country around you and the people in the town. Life and your experiences in your environment are similar to the aspect of the countryside from the speeding train. Your senses are barraged by such a multiplicity of sensations that you have only a hazy impression. If you do such a relatively simple thing as bake a cake, or walk in the garden, you experience an environment that is amazing in its complexity.

When a scientist uses the scientific method, he attempts to simplify the situation as completely as possible, so that he may consider and understand every facet of its variability. Thus before he can consider the problem of the cake, he must consider separately the composition of each ingredient, the effect of heat on each, their effect on one another, and many other problems. He must observe these simple relations over and over, so that he may be certain that he is correct in his conclusions.

Obviously, if a scientist were to tackle the problem of the cake and why it is delicious sometimes, and not on other occasions, it would take several lifetimes before he began to understand the full problem and its implications. Any scientist must therefore depend on the work which many, many others have done in the past and are doing today. The advance in the understanding and control of our environment has become more and more dependent on the cooperative effort of many scientists.

The scientific method involves three principles: (1) The observation of isolated and simple sections of our environment. (2) The repetition of observation to eliminate errors and caprice of observation and judgment. (3) Close cooperation of scientists.

What Is Our Physical World and How Is It Studied?

All the parts of our environment which are made up of matter or energy or both, comprise the physical world. *Matter* is defined as anything which occupies space. *Energy* is the ability to do work. This means that anything which you perceive through your senses such as heat and light, air in the movement of wind, the infinite number of objects, is all part of the physical world. Ideas of goodness, God, feelings of love and comradeship may be part of our environment but are not of the physical world.

Since scientists investigate very small segments of this complex physical world, science has been divided into categories, and an investigator usually spends his scientific life investigating phenomena in one category. The boundaries of these categories are not rigid and many scientists work on the borders. It is very difficult at times to say whether an investigator is a physiologist or a biochemist, a geologist or a physicist. The categories are shown.

The Natural Sciences

Biological Sciences

Botany
Bacteriology
Zoology
Psychology

Physical Sciences

Astronomy
Chemistry
Physics
Geology
Mathematics

There are fields of science to cover all the realms of experience with the physical world. It is *chemistry* which constitutes the knowledge of the composition of things, the forces which bring about changes in composition, and the results of these changes.

How Did the Knowledge of Chemistry Develop?

Archeologists believe that man has been on this earth perhaps 500,000 years, but knowledge of all except the last few thousand years is extremely scanty. No one knows how man developed or what his life was like long ago except from the few fragments which have been recovered from ancient graves, in caves, and around ancient home sites. History begins with the development of writing. In the period before writing, or the Prehistoric period, man had learned to carry out and control a number of processes

involving chemical reactions. He was able to make pottery and glass, to produce wine and vinegar, to dye cloth, to make soap, and to isolate copper from its ore. Probably these arts were accidentally discovered and accidentally improved. It is well known that knowledge of these operations among more recent people who do not have writing is handed on from father to son and that there is frequently a good deal of mysticism and superstition connected with these skills.

Four thousand years ago in the area of present day Egypt, Palestine, and Iraq, writing was developed and the historical period began. It was at this time that mathematics was started, that interest in the stars developed, and that the knowledge of the production of copper alloys, particularly that of copper and tin to form bronze, was acquired. This last development was a chemical process. The formation of alloys was not understood at that time, of course, but the fact that men could make tools out of a substance, bronze, which was superior to flint in many ways, had far reaching effects. The mining of copper and tin ore and the working of these metals influenced the development of trade,

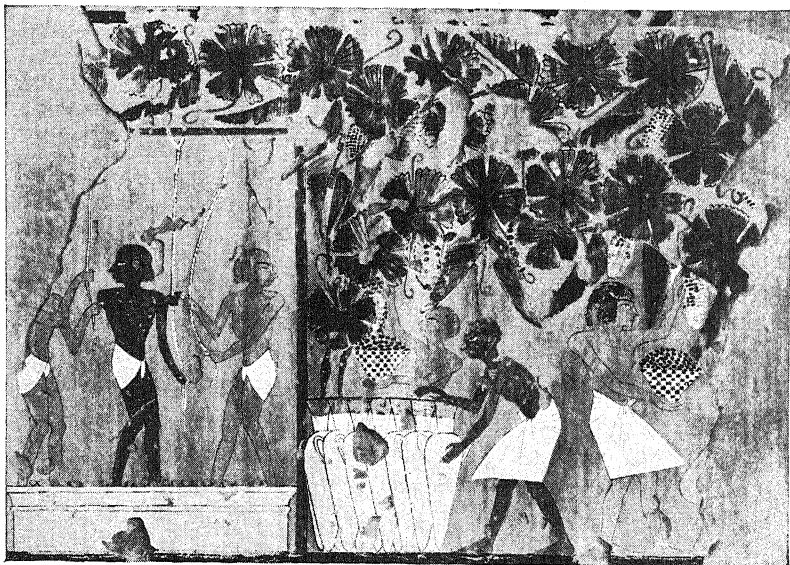


Fig. 1-1. Wine making, an ancient art allied to chemistry. Reproduction of an Egyptian wall painting, XIX dynasty—Thebes. (Courtesy of the Metropolitan Museum of Art.)

the founding of towns, and the interchange of products and culture in the succeeding era.

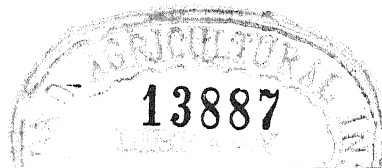
About a millennium later, iron was discovered, and the process for producing it from its ores, melting, and working it was mastered. The production of iron tools had as great an effect on the development of civilization as had the earlier production of bronze, the copper alloy.

So down through the ages, there are scattered records of the accidental discovery of a few chemical reactions and in some cases, of their profound effect upon the culture of the time.

The Greeks Although there developed in Greece a high civilization and there were many men interested in what our world is made of and why things change, there was little real development of science in those times. We can think of a few outstanding contributions to the development of science. Archimedes' principle for measuring the volume of an object by weighing it in air and then in water and the principle of the lever are two outstanding examples. But through the centuries of Greece's eminence, her scholars were more interested in speculation than in experimentation. The "elements" accepted by most Greek philosophers and used by them to explain the world, were "air," "earth," "fire," and "water." Some of them added the fifth, "essence." They believed that the different properties of the multitude of things in their environment derived from a difference in the proportions of these four or five "elements." But a science does not develop without experimentation, and therefore chemistry was not founded during this period of intellectual ferment.

Alchemy Before the fall of the Roman Empire, there began to develop in Mediterranean Africa and Europe a cult called Alchemy. This flourished through the Middle Ages and, indeed, remnants of it are still among us today.* The chief aims of these alchemists were (1) the transmutation of common materials into precious gold and (2) the discovery of a substance which would impart immortality ("The Elixir of Life"). Needless to say, these aims were never realized. But through the years, many individuals claimed to be able to achieve these difficult ends, and many more thought they were on the brink of discovering

* See *Time* Aug. 2, 1948. A description of "master cells," concrete disks which, it is claimed, cure anything.



how to do it. Their methods were filled with incantations, and superstitious ritual, but their methods did include many manipulations and actual work with materials. They mixed all sorts of things together and heated and distilled, froze and filtered them. They learned a crude kind of laboratory technique and they accidentally stumbled on some chemical compounds. For example, Brand, a German merchant, mixed phosphate rock, sand, and urine and distilled it. He produced phosphorus, the first isolation of that element. His mixture was one which was fairly typical of that which many alchemists used. It contained a common material — sand, a less common substance — phosphate rock, and the excrement of a living being — urine. Veneration for the mystical quality of the spark of life and for anything pertaining to it, was high, and frequently some part of an animal or its excrement was included in the pot. They had no way of regulating or recording pressure or temperature but attempted to control their mixtures by carrying out the opera-

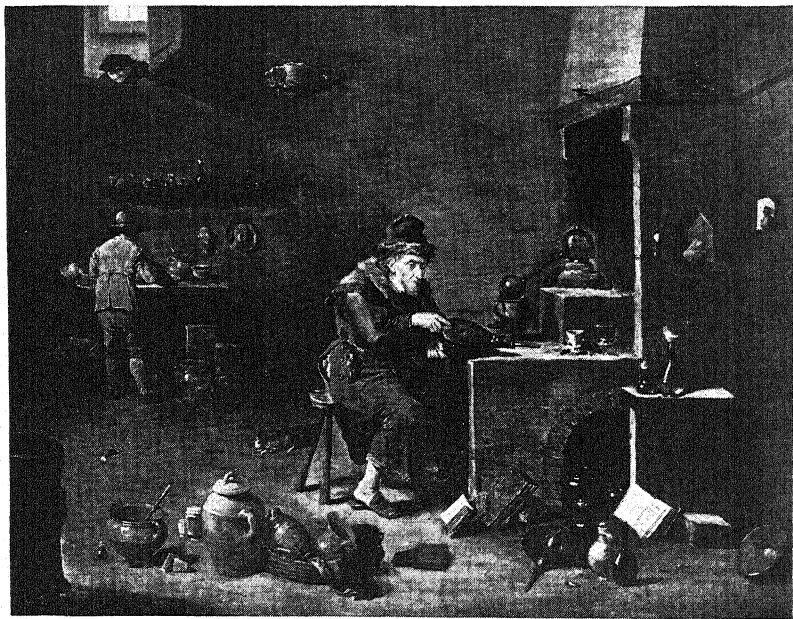


Fig. 1-2. The Alchemist. Reproduction of a painting by David Teniers (1610-1690). Notice the apparatus and the stove. (Courtesy of Fisher Scientific Company.)

tion in the "correct" phase of the moon, or when the position of the planets was "favorable," and with mystic incantations. It is difficult today to know exactly how they worked since the few records which they left are a jumble of words. The Emerald



Fig. 1-3. Alchemical symbols of some elements.

Tablet of Hermes Trismegistos was famed among alchemists for containing the basic secrets of alchemy. The legendary words have come down to us, but their meaning is obscure. In part it says,

"You will separate the earth from the fire, the subtle from the compact, gently, with great skill. It ascends from earth to Heaven, then descends again to earth and receives the force of those above and those below.

"Thus you will possess the glory of the whole world and all obscurity will flee from you."*

This scarcely sounds like a chemistry laboratory direction sheet. Nevertheless, although we cannot trace the development of methods and material, when the scientific era began to develop, certain knowledge had accumulated during the alchemical period. These accomplishments were (1) development of certain crude apparatus such as the retort and crucible, (2) the preparation and recognition of certain elements and compounds, such as sulfuric acid, copper sulfate, and calcium oxide, but particularly (3) an interest in experimentation.

The Renaissance You are familiar with the exciting history of the Renaissance and the profound influence which this intellectual development has on events today. You know of the renewed interest in Greek and Roman literature, the rebellion against authority and the beginning of recognition of the individual, the theological arguments and schisms, the interest in graphic and plastic arts, the voyages of discovery, and the invention of the printing press which occurred in the fifteenth

* From *A History of Chemistry*, by F. J. Moore. Copyright, 1918. Courtesy of McGraw-Hill Book Co.

century. The science of chemistry had its roots in these stirring times. But several centuries passed before the scientific method began to be used knowingly and the superstitions of alchemy were eliminated from the laboratory.

An example of a worker of those times is Johann Glauber (1604–1668), a German dispenser of secret medical preparations. He believed and followed many of the alchemical superstitions, and yet he was a keen, brilliant observer. We still call sodium sulfate, Glauber's salt. He showed that it can be prepared from the reaction of sodium chloride and sulfuric acid. He studied other reactions and correctly interpreted their course. He prepared nitric acid from nitrates and acetic acid by the distillation of wood.

Robert Boyle (1627–1691) contributed much to the discarding of alchemical tradition. You are doubtless familiar with his name in connection with the properties of gases, since he discovered the law that the volume of gas varies inversely as the pressure on it (Boyle's law). In 1661, he published *The Skeptical Chymist*, one among his many works. (*The Skeptical Chymist* was reprinted in 1937 by E. P. Dutton and Company, New York, and you may find copies of it in many libraries.) In this book, he challenged the hypotheses current at that time, that matter was composed of either three or five basic elements ("a saline, a sulphureous and mercurial part" or "five differing substances — salt, spirit, oyle, phlegme, and earth"), and criticized the experimental evidence for these hypotheses. At that period, the difference between a physical change such as liquid to gas and a chemical change such as carbonate to oxide was not understood. Boyle did not set things straight nor could he perceive what modern theory has achieved, but the scorch of his criticism opened the door to truer interpretations of the nature of matter.

Gradually in all the sciences, chemistry among them, the scientific method of controlled experiment, careful observation, adequate number of samples, and precise recording emerged.

Today the scientific method is applied in thousands of laboratories all over the world, and the products of these laboratories affect our pattern of living. Unfortunately the scientific method is not yet used to any extent in our daily life.

NEW TERMS

Matter, energy, physical world, chemistry, alchemy, science.

QUESTIONS

1. Describe the steps used in the scientific method.
2. How did it happen that the science of chemistry developed?
3. What were the contributions of alchemy?
4. Does the development of chemistry parallel similar developments in other fields? Explain.

Physical World

You are living in a physical world which is bombarding your senses with perceptions. You feel a hard stone, you see green grass, you smell turpentine, you feel a cold wind. Your senses and the sensations which they allow you to experience give you knowledge of this physical world. (Of course you must experience sensations common to other people — pink elephants do not count.) When an evaluation of sensations and an attempt to sort them are made, this world appears made up of *matter* and of *energy* so closely associated that it is difficult to separate them. Let us try to define these two aspects of our physical world and see if, through the test of your own experience, they are actually different, and if they cover all your sensations. Matter is commonly defined as *anything which occupies space*. Energy is defined as *the ability to do work*.

Experience tells you that matter may be solid, liquid, or gaseous. The *properties* of matter, the characteristics which identify substances are manifold and very different. Things differ in color, odor, state of division, density, elasticity, and may have other properties. (You can think of others.) Energy is experienced in the form of heat, light, electricity, and motion. Not only can matter give off or take on energy, but it may also be in a state where it is not giving off energy, but has the ability to give off energy. The battery in a car can be made to give off electricity; the coal in a bin can be made to give off heat and light; the food you eat can be made to give off heat and motion; the water above a dam may fall over and give off motion. These are forms of *potential energy*. In the first three examples the potential energy was *chemical energy*, energy held in the compounds. *Potential energy is energy which is stored*. *Chemical energy is potential energy which is stored in chemical compounds*.

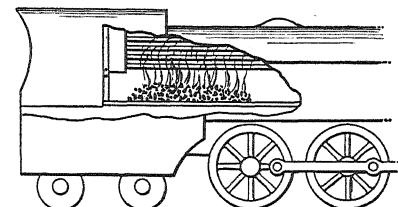
For several centuries it was believed that matter and energy could neither be produced nor destroyed. These ideas were embodied in the Law of Conservation of Matter and the Law of Conservation of Energy and test after test showed them to be true. The Law of Conservation of Matter states that matter may neither be created nor destroyed. The Law of Conservation of Energy states that energy may neither be created nor destroyed.

Today we know that occasionally matter and energy may be changed into one another. The source of the tremendous

E N E R G Y



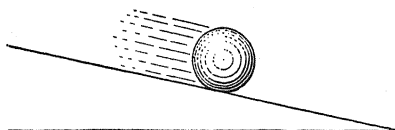
Kinetic energy of gases



Heat

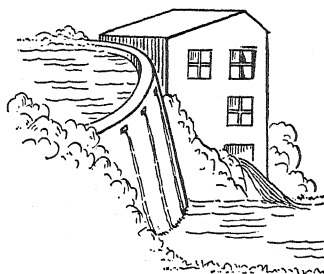


Light

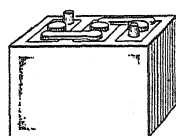


Motion

MANIFEST



Water behind dam



Storage battery



Food

POTENTIAL

Fig. 2-1.

amount of energy released in an atomic bomb is the destruction of a very small amount of matter. So far no one has changed a large amount of energy into a small amount of matter. In our daily life, the Law of Conservation of Matter and the Law of Conservation of Energy are still inviolate.

Composition of Matter

When the objects encountered in daily life are analyzed chemically, it is found that a few are pure substances, but most are mixtures. A *pure substance* is a material which is completely homogeneous to the most minute survey. It cannot be separated by physical means. There are few pure substances in your daily life. Salt, sugar, and baking soda which you use in your home, are almost pure substances, but even salt usually has a small amount of drying agent added to prevent it from caking, and iodized salt has a small amount of sodium iodide. Even the metals which you use are commonly mixtures. Your gold ring contains copper and probably silver as well as gold. The aluminum in your cooking pans is not pure but alloyed and is thereby more rigid and stable than pure aluminum.

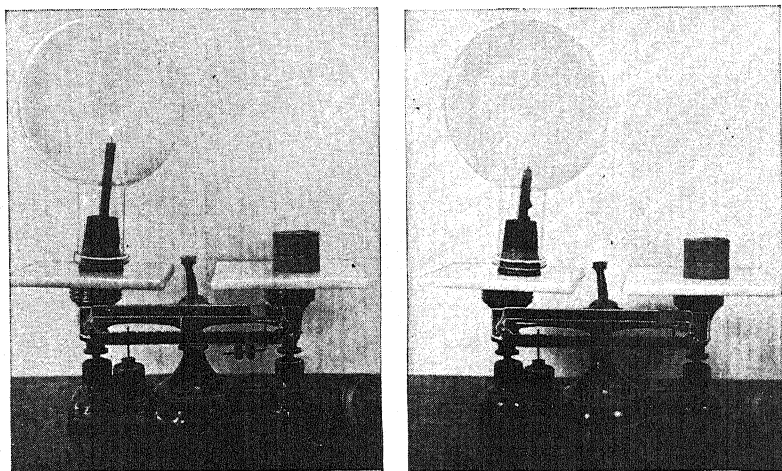


Fig. 2-2. The Law of Conservation of Matter. Early investigators did not recognize the Law of Conservation of Matter because a candle disappears as it burns. We can show that it does not disappear by capturing the products of the burning. In the first picture a burning candle in a flask is balanced against weights. When the candle goes out, the pans are still balanced. There has been no loss in weight although the size of the candle is smaller.

When matter is observed under as simple a situation as possible and under a great variety of conditions, it becomes apparent that all matter is composed of tiny particles held together more or less compactly. This is true of solids, liquids, and gases. Carry out a few experiments and then try to explain them. Take a small bottle of hydrogen sulfide gas, the gas which smells like rotten eggs, and release it by uncovering the bottle in the largest room in the building. Now leave the room for a few minutes so that your sense of smell will not be fatigued. Come back in five or ten minutes, and sniff the air in each corner of the room. It smells like hydrogen sulfide. How can you explain this? You must conclude that the gas is made up of particles which were close together in the bottle (the odor was stronger) and moved out into the room.

You can observe the same thing with some solids. Have you ever put a handful of moth crystals, either *para*-dichlorobenzene or naphthalene, in a clothes closet? When you open the door the closet is filled with the odor of the crystals.

Or do this experiment. Take a few small crystals of a highly colored solid such as potassium permanganate and dissolve them in a rather large volume of water, say 500 milliliters. The solution will be purplish pink. Then pour a small amount of this solution into a large amount of water. Continue diluting the solu-

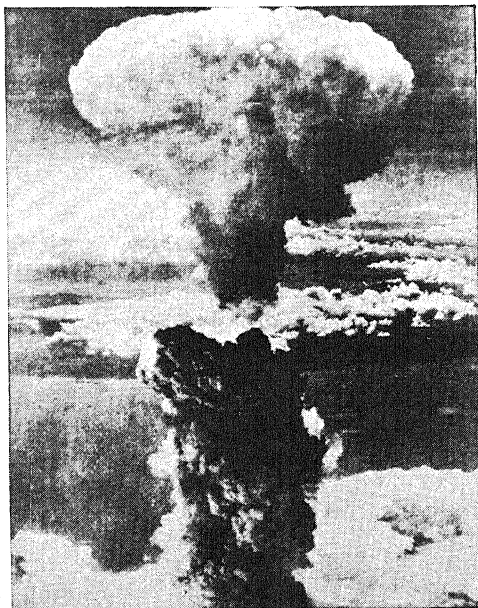


Fig. 2-3. Burst of the atomic bomb over Nagasaki. (Courtesy of War Department, Manhattan Project.)

tion until the pink color of the potassium permanganate can no longer be seen. You will be amazed at the large volume of water which can be colored by a few small crystals. How is this possible? The only plausible explanation which has ever been devised is that these crystals are made up of many, many tiny particles all the same color.

Of the things encountered in daily life, a few are made up of particles which are all alike. These are the pure substances.

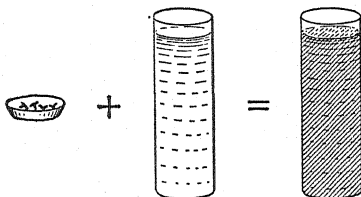


Fig. 2-4. A very few crystals of potassium permanganate are able to impart a purple color to a large volume of water.

Most are made up of mixtures of different particles. But everything, whether solid, liquid, or gas, is composed of particles.

Elements The basic units in all matter are the elements. An *element* may be defined as a substance which cannot be subdivided by any ordinary chemical or physical means. It can now be subdivided by atomic bombardment — atom smashing — but this is no “ordinary” means. The number of elements in our environment is 88,* some of which are very abundant and present in most of the material which we encounter, such as oxygen, and some of which are very rare. The atomic physicists have now prepared six new elements heavier than any yet known and the new table of elements now contains 98. Some of the substances in our environment are free elements, as the oxygen of the air, while some are composed of different elements held together chemically. When elements are held together chemically the substance is called a *compound*. For example, cotton is a mixture of pure substances, with the most abundant one composed of three elements, carbon, oxygen, and hydrogen, held together chemically.

But you don’t know what is meant by this term “held together chemically.” Let us explain the difference between a compound in which elements are “held together chemically” and a mixture of elements.

* Four of the elements usually listed with the 92 natural elements of our environment are so unstable that it is unlikely that they have existed naturally in historical time.

Compounds Suppose two pure elements, zinc and sulfur, are ground together. At first with the naked eye, you can see the distinct particles of gray zinc and yellow sulfur. You know this is a *mixture* of two substances since you can see that it is *heterogeneous*. As grinding continues and the particles become smaller, the material appears a yellowish gray and to the naked eye looks homogeneous. But with a magnifying glass particles of sulfur distinct from the particles of zinc can still be seen. If this mixture is stirred into a liquid, carbon disulfide, the sulfur will dissolve and the zinc will fall to the bottom. The two elements will be separated by solution, a physical process. Also the mixture will react with hydrochloric acid to produce hydrogen just as zinc does. All of the properties, either physical or chemical, will reflect the presence of sulfur and zinc. Furthermore there was no change of temperature when the mixture was formed. In other words, no heat was given off or taken on.

Now prepare a compound of zinc and sulfur, a substance in which the elements zinc and sulfur are *held together chemically*. This compound is prepared by heating a mixture containing approximately twice the weight of zinc as of sulfur in a crucible or on an asbestos board. Suddenly as the mixture is heated, there is a blinding flash, the mixture glows hotly and then, since the flame has been removed, cools down. The two elements *have combined chemically*. (Not all combination is so spectacular.)

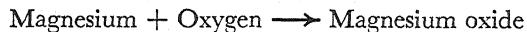
How does the compound compare with the mixture of elements? First the color of the compound is much lighter. It is a creamy white, while the mixture was yellowish gray. If other properties are tested they, too, are found to be different. The compound will not dissolve in carbon disulfide. When hydrochloric acid is added, instead of forming odorless hydrogen, it produces a gas which smells like rotten eggs, hydrogen sulfide. Second, it is impossible to find any physical means, solution, distillation, melting, centrifuging, etc. which will accomplish the separation of the sulfur and zinc. Third, when the compound was formed, heat and light were given off. The fourth difference is one which, at present, it would be difficult for you to observe, that is, the amounts of zinc and sulfur present. The compound has a definite amount of zinc, 2.039 grams, for each gram of sulfur. In the mixture there may have been any amount, from low to high, of zinc per gram of sulfur but the compound always

has a definite quantity. This illustrates the difference between a mixture of elements and a compound, elements held together chemically.

<i>Mixture</i>	<i>Compound</i>
1. Properties are the sum of properties of components	Properties are distinct
2. Can be separated by physical means	Cannot be separated by physical means
3. No change in energy on formation	Energy is given off or taken on, when it is formed
4. Has variable composition	Has definite composition

Chemical Change and Physical Change

Most things in our physical world are frequently undergoing change — the most common experience is that of *change* in things. All these changes are either physical changes or chemical changes. *A physical change is a change in the state or structure of matter, while a chemical change is a change in the composition of matter.* How can they be distinguished? How can one recognize when a chemical change is taking place or when it is a physical change? There are two striking types of change which indicate that a chemical change or chemical reaction has occurred. One is an extensive change in properties, and the other is the gain or loss of energy. Both must be used with caution, however, in interpreting results since physical changes may be sometimes accompanied by such manifestations. If a shiny, metallic magnesium ribbon is heated, it will suddenly begin to burn with a bright blinding flame and will change to a white powdery ash. This is clearly a chemical change since the properties are altered markedly and energy (heat and light) has been given off. If a shiny platinum wire is heated, it will glow with a red color. But when it is removed from the flame, it regains its original properties. This is undoubtedly a physical change. When these two changes are more carefully studied, it is found that the magnesium has undergone a change in composition while the platinum has not. Magnesium oxide has been formed through a chemical reaction:



Occasionally one property of a substance may be altered during a physical change. For example, vaporizing water is a

physical change which does alter the state of the water, one of its physical properties. But it does not alter the other properties of water. If most of the properties of a substance are unaltered or regained, the change is likely to be a physical change and not a change in composition. Occasionally a release of heat accompanies a physical change. Friction generates heat but does not result from chemical changes. These two criteria — change in properties and release or consumption of energy — will differentiate a chemical change from a physical change. But they must be used with care.

Molecule If a gram of zinc sulfide, the compound of zinc and sulfur which has just been discussed, is prepared, and it is divided in two, each half gram will have the same properties. Or if it is divided into one hundred parts, each centigram (0.01 gram) will have the same properties. If it were repeatedly divided until an extremely small particle was obtained which had all the properties of zinc sulfide but which could not be further divided without losing these properties, this would be a *molecule*. *A molecule is the smallest particle of a compound or element which retains all of its properties.*

The size of molecules is extremely small. They vary in size with the composition of the molecule, so that a molecule of water is very much smaller than a molecule of rubber. The spaces between the molecules may also vary considerably in size. Let us give you an idea of their size. There are 6.02×10^{23} molecules (Avogadro's number = 602000000000000000000000) in 18 grams of water or 342 grams of table sugar. Pour out 18 grams of water. It will be approximately 18 milliliters or not quite two teaspoons of water. All these molecules in such a little volume! The sugar, 342 grams, will occupy about three cups for the same number of molecules.

Atoms If each of these compounds, water and sugar, is analyzed, it is found to contain the elements hydrogen and oxygen for water and hydrogen, oxygen, and carbon for sugar. We may easily demonstrate this. If an electric current is passed through water which contains a small amount of sulfuric acid to carry the current, hydrogen and oxygen gas are formed. (These gases are elements and there is no decomposing or simplifying them.) If a molecule of water is a very small particle which retains all the properties of water, then it seems logical to

conclude that a molecule of water is composed of hydrogen and oxygen. These small bits of elements which are combined chemically to form molecules are called *atoms*. *An atom is the smallest particle of an element which enters into chemical combination.* There may be one or more atoms of various elements in a molecule. Thus it can be shown by experiment (but has not been demonstrated to you) that a molecule of water contains two atoms

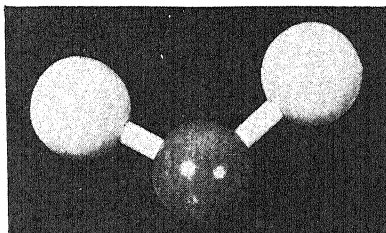


Fig. 2-5. A molecule of water, H_2O , contains two hydrogen atoms and one oxygen atom. The model shows the arrangement of the atoms in the molecule.

of hydrogen and one atom of oxygen. A sugar molecule contains twelve atoms of carbon, twenty-two of hydrogen, and eleven of oxygen.

Atomic and Molecular Weights

The atoms of different elements vary from one another in many respects, one of which is the average weight of the atoms. If it were possible to weigh ten atoms of sulfur they would weigh twice the amount of ten atoms of oxygen and therefore the average weight of one atom of sulfur is twice the average weight of one atom of oxygen. Of course, it is not possible to weigh ten atoms of any element since this is by far too small a quantity for anyone to handle. It is possible to weigh rather large numbers of atoms and compare their weights. Thus it is found that a million atoms of copper weigh almost four times as much as a million atoms of oxygen. It is not possible to weigh *one* atom of any element and assign a weight to it in any system which would have much meaning. But it is possible to assign relative weights to elements. Oxygen is the reference element and it is assigned a value of 16. This means then that sulfur is approximately 32 and copper approximately 64. (Accurately $S = 32.06$ and $Cu = 63.57$.) *The atomic weight of an element is the relative weight of that element compared to oxygen as 16.* (Some other weight

than 16 might well be assigned to oxygen. Atomic weights were once used in some laboratories on the basis of oxygen as 100. However with oxygen as 16, hydrogen, the lightest weight element, is approximately 1 — accurately 1.008. This system is now used internationally.)

The molecular weight of a pure substance is the relative weight of one molecule compared to the weight of the oxygen atom as 16. Thus the molecular weight of water is then 18 since it contains two hydrogen atoms and one oxygen atom.

Gram Atomic Weight and Gram Molecular Weight

The *gram atomic weight* is the atomic weight expressed in grams. Thus the gram atomic weight of oxygen is 16 grams. This is sometimes called *one gram atom*. Two gram atoms, or gram atomic weights, of oxygen are 32 grams. A gram molecular weight is the molecular weight expressed in grams. Thus a *gram molecular weight* of water is 18 grams. This is sometimes called a *mole*. Two gram molecular weights of water, or two moles, are 36 grams of water.

Ions

An *ion* is an atom or a group of atoms which contains a low positive or negative charge. The atoms in inorganic compounds usually exist as ions.

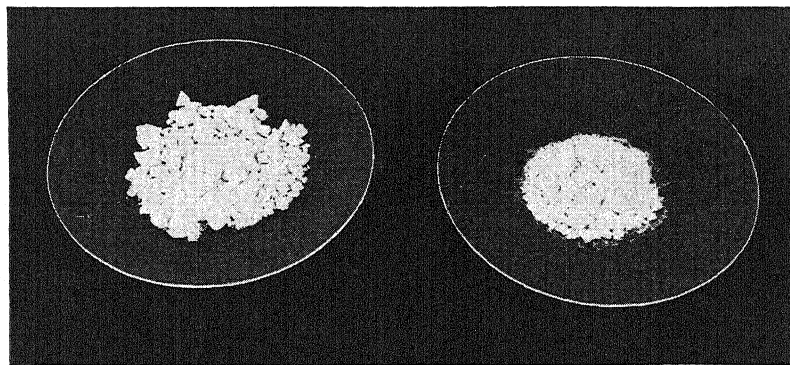


Fig. 2-6. A gram molecular weight (1 GMW) of sulfur weighing 32 grams is shown on the left. One half a gram molecular weight ($\frac{1}{2}$ GMW) of sulfur weighing 16 grams is shown on the right.

Symbols and Formulas

Chemists use a kind of shorthand for indicating one or more molecules of a certain substance. For this "shorthand" there has been assigned to each element a symbol, O for oxygen, Cr for chromium, Na for sodium, etc. The symbol is composed of a capital letter and sometimes one small letter. It is derived from the name of the element. Thus O is the first letter of the name oxygen. If a new element were given a name beginning with O, its symbol would contain two letters, O and probably the second letter. Chromium has the symbol "Cr" rather than "Ch" because the word "chlorine" also starts the same way. Chlorine's symbol is then "Cl." A few elements, such as sodium, have symbols which do not appear to be related to the name. These symbols are derived from other names for the element, usually Latin names. Thus the Latin name for sodium (Na) is "natrium," for silver (Ag), "argentum."

Formulas are written for one molecule of a pure substance. The formula of a compound indicates *the elements present in one molecule of that substance and the number of atoms of each element present*. The number of atoms of each element is indicated by writing a subscript number, immediately following the symbol. Thus the formula H_2O , indicates that in one *molecule* of the pure substance water there are *two atoms* of hydrogen (H) and one atom of oxygen (O). The formula Na_2CO_3 indicates that one molecule of sodium carbonate contains two atoms of sodium (Na), one atom of carbon (C), and three atoms of oxygen (O).

When brackets or parentheses are used and a subscript number is placed immediately outside the bracket, everything inside is multiplied by that subscript. Thus $\text{Ca}(\text{OH})_2$ indicates that one molecule of calcium hydroxide contains one atom of calcium (Ca), two atoms of oxygen (O), and two atoms of hydrogen (H).

A number placed *in front* of a formula indicates the number of molecules of that substance. Thus 2NaCl indicates two molecules of salt, each molecule of which contains one atom of sodium (Na) and one atom of chlorine (Cl) or $3\text{H}_2\text{O}$ indicates three molecules of water, each molecule of which contains two atoms of hydrogen (H) and one atom of oxygen (O).

Deduction of Formulas The formulas of pure substances are deduced by (1) analyzing the compound quantitatively and

(2) determining the molecular weight. It is not possible, at this point, to explain simply and adequately how a compound may be analyzed. This involves chemical procedures to determine accurately the amount of each element in a pure substance. Likewise it is difficult to explain, at present, how molecular weights may be determined. Several methods will be studied later on. None of these methods is accurate, but they do give an indication of the molecular weight.

Determined (1) % composition, (2) molecular weight.

Calculate molecular formula.

$$\begin{aligned} \text{Molecular weight} \times \% \text{ Composition} \\ = \text{Weight of element in 1 gram molecular weight} \end{aligned}$$

The weight of the element present in one gram molecular weight will be equal to the atomic weight if there is only one atom in each molecule or a multiple depending on the number present.

Divide the *weight* of the element in one gram molecular weight of compound by the atomic weight of the element to determine the number of atoms of the element in the compound.

EXAMPLE: The molecular weight of methane is 16. On analysis it is found to contain 75.00% carbon and 25.00% hydrogen.

$$\begin{aligned} \text{Carbon } 16 \times 75\% &= 12 \text{ g. of carbon} \\ \text{Hydrogen } 16 \times 25\% &= 4 \text{ g. of hydrogen} \\ 12 \text{ g.} \div 12 \text{ (gram atomic weight of C)} &= 1 \text{ atom} \\ 4 \text{ g.} \div 1 \text{ (gram atomic weight of H)} &= 4 \text{ atoms} \\ \text{Formula} &= \text{CH}_4 \end{aligned}$$

Empirical Formula The empirical formula of a compound shows the elements which are present and the *ratio* of atoms of the elements. A molecular formula shows the actual *number* of atoms of each element. Thus, the molecular formula for hydrogen peroxide is H_2O_2 , since in each molecule there are 2 atoms of hydrogen and 2 of oxygen. The empirical formula for hydrogen peroxide is HO. This shows that the compound is made up of hydrogen and oxygen and that in a molecule the ratio of hydrogen atoms to oxygen atoms is 1:1. The empirical formula does not tell as much as the molecular formula, but when it is

not possible to determine the molecular weight, it is the best that can be done.

Examples of Molecular and Empirical Formulas:

<i>Compound</i>	<i>Molecular Formula</i>	<i>Empirical Formula</i>
Benzene	C_6H_6	CH
Acetic acid	$C_2H_4O_2$	CH_2O
Sodium chloride	NaCl	NaCl
Ether	$C_4H_{10}O$	$C_4H_{10}O$

The empirical formula can be calculated from the percentage composition of the compound. If the amount of each element in a given quantity of the compound, say 100 grams, is divided by the atomic weight of that element, the ratio of the atoms in the compound will be obtained in terms of fractional numbers. The fractional number ratios can be converted to whole number ratios by dividing the smallest fraction into the others. Occasionally even this will not result in whole numbers, but further multiplication by 2 or 3 will give whole numbers.

PROBLEM: A compound is found, on analysis, to be composed of 52.17% carbon, 13.04% hydrogen, and 34.78% oxygen. Calculate the empirical formula.

ANSWER: Calculate the number of grams of each element in 100 g. of compound and divide by the atomic weight of that element:

$$\begin{array}{rcl} \text{C} & 52.17 \text{ g.} \div 12 & = 4.34 \\ \text{H} & 13.04 \div 1 & = 13.04 \\ \text{O} & 34.78 \div 16 & = 2.17 \end{array}$$

In other words, our ratio is 4.34 atoms of carbon:13.04 atoms of hydrogen: 2.17 atoms of oxygen. To simplify the ratio, divide each number by the smallest one, 2.17:

$$\begin{array}{rcl} \text{C} & 4.34 \div 2.17 & = 2 \\ \text{H} & 13.04 \div 2.17 & = 6 \\ \text{O} & 2.17 \div 2.17 & = 1 \end{array} \quad \text{Empirical formula: } C_2H_6O$$

Writing Formulas The atoms in most inorganic compounds exist as ions, and in one molecule the total number of positive charges is equal to the total number of negative charges. When elements form ions, they tend to have one or at most two valences. *The valence of an ion is the charge on the ion, a measure of*

its chemical combining power. If the valences of the ions which make up a compound are known, it is then possible to write its formula.

Chemists were not able to predict the valence of an element, but had to work through two centuries before they discovered what the valence of each element tends to be. Some elements are always plus one when they combine and form compounds. Others are always plus two. Some elements show variable valence; in one group of compounds they may have one valence, and in another group of compounds, they will have a second valence. Iron is an example of an element which shows variable valence. In some compounds of iron, the valence is plus three, while in others it is plus two. Iron never exists as plus one or with a negative valence. Different names are used for the iron which is plus two and that which is plus three. The iron with the lower valence is called "ferrous" and that with the higher plus three valence is called "ferric."

Sometimes a group of atoms will move through a solution together and will enter into chemical reactions as one unit. This group of atoms has a charge and is an ion with its own characteristics. These groups of atoms which constitute an ion are called *radicals*. One example of a radical is the hydroxyl ion which is composed of an oxygen and a hydrogen atom with a total charge of minus one. It is written OH^- . There are other common examples in the chart.

Ions

H^+ hydrogen	Cl^- chloride
K^+ potassium	Br^- bromide
Na^+ sodium	I^- iodide
Ag^+ silver	OH^- hydroxide
NH_4^+ ammonium	NO_3^- nitrate
Ca^{++} calcium	$\text{C}_2\text{H}_3\text{O}_2^-$ acetate
Mg^{++} magnesium	O^- oxide
Zn^{++} zinc	S^- sulfide
Cu^{++} copper (cupric)	CO_3^- carbonate
(Cu^+ is cuprous, but is not very common.)	
Fe^{++} ferrous } iron	SO_4^- sulfate
Fe^{+++} ferric } iron	PO_4^- phosphate
Al^{+++} aluminum	SO_3^- sulfite

Sodium chloride is then Na^+Cl^- or the formula is NaCl . Calcium chloride has a positive ion (called cation) with a plus two valence (Ca^{++}) and a negative ion (called anion) with a

minus one valence (Cl^-). If the total number of positive charges is equal to the total number of negative charges in one molecule, then there are two chlorides each with a negative one. (The formula for calcium chloride was experimentally determined long ago by the method indicated above.) The formula is therefore CaCl_2 . Aluminum oxide has aluminum ions, plus three, and oxide ions, minus two. The least common multiple of two and three is six. There must be then two aluminum ions for a plus six charge, and three oxygen ions for a minus six. The formula is Al_2O_3 .

The formula is written with the positive ion placed first, followed by the negative ion, and it is named in the same sequence.

Naming All the rules for naming compounds are not presented. More will be given later. The rules are:

1. Give the name of the positive element.
2. For binary compounds, compounds with only two elements, give the root of the name of the negative element and add "-ide."
3. For compounds containing more than two elements, there will usually be a *radical*. Give the name of the radical. (A *radical* is a group of atoms acting together as one ion. Examples: NH_4^+ , $\text{SO}_4^{=}$)
4. Compounds which have a hydrogen ion as the positive ion, are acids. They are named by giving the root of the negative radical and changing "-ate" to "-ic" and adding acid — HNO_3 , nitric acid. When the ending is "-ite," it is changed to "-ous" — H_2SO_3 , sulfurous acid.
Binary acids are named "hydro---ic" — HCl , hydrochloric acid.

Formulas of Elements The formulas for free elements which are solids and for the liquid metal, mercury, are composed simply of the symbol of the element. This indicates that there is only one atom to each molecule. On the other hand the gaseous elements with the exception of the Rare Gases (helium, neon, argon, krypton, and xenon) contain *two* atoms to the molecule. This is also true of bromine and iodine which vaporize readily at room temperature. The complete list of elements which contain two atoms in each molecule is: hydrogen, H_2 ; oxygen, O_2 ; nitrogen, N_2 ; fluorine, F_2 ; chlorine, Cl_2 ; bromine, Br_2 ; iodine, I_2 .

Write all other elements with one atom to the molecule. In the discussion of oxygen (Chapter 5) and of hydrogen (Chapter 6), some proof of the occurrence of two atoms to the molecule will be given.

NEW TERMS

Matter, energy, property, potential energy, chemical energy, element, compound, chemical change, physical change, molecule, atom, atomic weight, molecular weight, gram atomic weight, gram molecular weight, symbol, molecular formula, empirical formula, binary compound.

QUESTIONS

1. What is the difference between matter and energy?
2. How can you tell the difference between a chemical change and a physical change? Which of the following changes are chemical?
 - a. The formation of gas when water is added to baking powder.
 - b. The burning of leaves.
 - c. The melting of ice.
 - d. The solidification of paraffin on top of jelly.
 - e. Boiling water.
 - f. Browning of meat.
 - g. Bleaching clothes.
 - h. Washing clothes.
3. How many atoms and what elements are in the following compounds: NaNO_3 , K_3PO_4 , NH_4Cl , Fe_2O_3 , NaHCO_3 , $\text{Mg}(\text{NO}_2)_2$, $\text{HC}_2\text{H}_3\text{O}_2$, $\text{Al}_2(\text{SO}_4)_3$, $\text{Ca}_3(\text{PO}_4)_2$?
4. How many molecules and what composition are the following: $3\text{H}_2\text{O}$, $4\text{Fe}(\text{NO}_3)_2$, 6O_2 , $2\text{H}_2\text{SO}_4$, 3HCl ?
5. Calculate the molecular weight of CaO , Na_2S , HNO_3 , $(\text{NH}_4)_2\text{SO}_4$, Fe_2O_3 . Calculate the gram molecular weight. What is the significance of the difference?
6. What is Avogadro's number? How many molecules are present in one gram molecular weight of H_2SO_4 ? In two gram molecular weights?
7. Write the formulas for the following compounds of sodium: the nitrate, the oxide, the chloride, the sulfate, the carbonate, the hydroxide, and the phosphate. Do the same for the compounds of calcium, of ferrous iron, of aluminum, and of silver.
8. What is a compound? How does it differ from a mixture?
9. What is the difference between a molecule and an atom? How many atoms are in a molecule?

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10. Calculate formulas for the following compounds whose percentage composition is given. Indicate whether the formula is an empirical or molecular formula.

<i>a</i>		<i>b</i>		<i>c</i>	
Magnesium	25.57%	Sodium	36.49%	Potassium	26.585%
Chlorine	74.43	Sulfur	25.43	Chromium	35.390
		Oxygen	38.08	Oxygen	38.025
<i>d</i>		<i>e</i>		<i>f</i>	
Calcium	38.72	Carbon	77.34	Carbon	71.96
Phosphorus	20.00	Hydrogen	7.58	Hydrogen	6.72
Oxygen	41.28	Nitrogen	15.08	Oxygen	21.32
		<i>Molecular</i>		<i>Molecular</i>	
		<i>Weight</i>	93	<i>Weight</i>	150
<i>g</i>		<i>h</i>		<i>i</i>	
Carbon	58.33	Carbon	75	Carbon	80
Hydrogen	4.07	Hydrogen	25	Hydrogen	20
Nitrogen	11.39	<i>Molecular</i>		<i>Molecular</i>	
Oxygen	26.01	<i>Weight</i>	16	<i>Weight</i>	30
	<i>Molecular</i>				
	<i>Weight</i>				
	123				
<i>j</i>		<i>k</i>		<i>l</i>	
Carbon	92.2	Carbon	25.00	Chlorine	52.56
Hydrogen	7.8	Hydrogen	8.33	Oxygen	47.44
	<i>Molecular</i>	Sulfur	66.67		
	<i>Weight</i>				
	78				
<i>m</i>		<i>n</i>		<i>o</i>	
Hydrogen	1.25	Arsenic	75.73	Carbon	66.67
Phosphorus	38.75	Oxygen	24.27	Hydrogen	7.41
Oxygen	60.00			Nitrogen	25.92
				<i>Molecular</i>	
				<i>Weight</i>	108

11. Write formulas for sodium chloride, magnesium nitrate, potassium phosphate, zinc sulfide, mercuric carbonate, aluminum sulfate, ferrous phosphate.
12. Square off paper with six vertical and six horizontal lines to form 25 squares. Across the top, put the positive ions — ammonium, hydrogen, calcium, cupric, and ferric. Along the side put the negative ions — nitrate, hydroxide, sulfate, oxide, and phosphate. Write the formula for the compound with the positive ion and negative ion indicated in each square.

Units of Measurement

Many of the observations which are made in a chemical laboratory are quantitative, that is, things are measured exactly. Therefore, the systems of measurements commonly used in chemistry and other sciences will be considered briefly.

The English system of weights and measures is a clumsy one. One-half of a yard is 18 inches; one-half of a pound is 8 ounces; one mile is 5280 feet. The metric system, on the other hand, is remarkably easy to use since it is founded on a system of tens, a decimal system. It is as easy to deal with meters and fractions of meters as it is to deal with dollars and cents.

Distance

The fundamental unit of the metric system is the meter. This is an international standard unit about the size of our yard (meter = 39.37 inches). It was intended when the metric system was proposed in France in 1791, that the meter would be defined

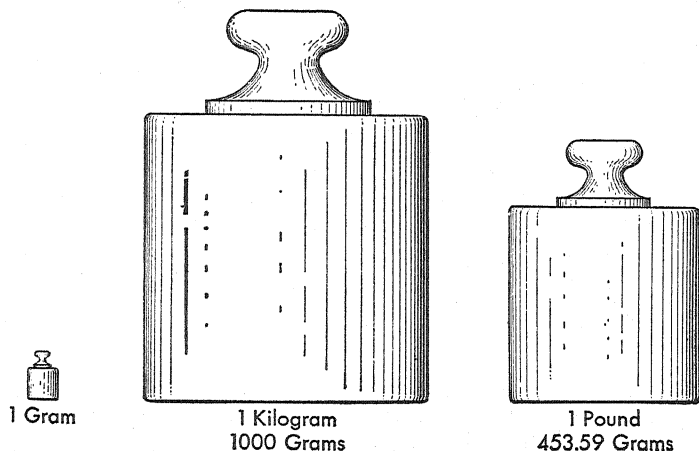


Fig. 3-1.

as one ten millionth of a quadrant of a meridian of the earth. An international treaty in 1875 redefined the meter in terms of a standard bar made of platinum and iridium and maintained under carefully controlled conditions. It can also be defined in terms of wavelength of light. Prefixes to meter indicate fractions or multiples of it.

kilo = 1000, therefore kilometer (km.) = 1000 meters (m.)

deci = $\frac{1}{10}$, therefore decimeter (dm.) = 0.1 meter (m.)

centi = $\frac{1}{100}$, therefore centimeter (cm.) = 0.01 meter (m.)

milli = $\frac{1}{1000}$, therefore millimeter (mm.) = 0.001 meter (m.)

Thus if a distance of 2 kilometers, 3 meters, 15 centimeters, 7 millimeters is measured, the total distance may be readily calculated. This is far simpler than the calculations one would make in using the English system.

$$\begin{array}{rcl}
 2 \text{ kilometers} & = & 2000 \quad \text{meters} \\
 3 \text{ meters} & = & 3 \quad \text{meters} \\
 15 \text{ centimeters} & = & 0.15 \text{ meter} \\
 7 \text{ millimeters} & = & 0.007 \text{ meter} \\
 & & \hline
 & & 2003.157 \text{ meters}
 \end{array}$$

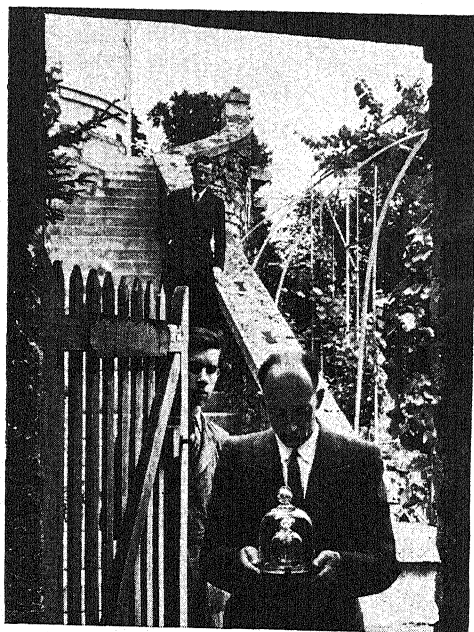


Fig. 3-2. The working kilogram at the International Bureau of Standards. This is the reference weight for all weights of the metric system. The master kilogram is kept in a vault and has not been used since before 1900. (Courtesy of Joe Pazen, Black Star.)

Weight

The standard unit of weight is the gram, a small weight used in careful measurement. The gram was originally defined as the weight of one cubic centimeter (a cube 1 centimeter by 1 centimeter by 1 centimeter) of water at maximum density (4°C.). It is now defined as one-thousandth of a standard kilogram which is kept at the International Bureau of Weights and Measures. A duplicate is in the United States Bureau of Standards. The same prefixes are used to indicate multiples.

When extremely small quantities such as the amount of a vitamin in a glass of milk are weighed, the microgram ($\mu\text{g.}$) or gamma (γ) is used.

1 microgram ($\mu\text{g.}$) = 0.001 milligram (μ is the Greek letter "mu" and γ is the letter "gamma").

Volume

The standard unit of volume is the liter. This is a little larger than our quart. The same prefixes are used here.

$$\text{Milliliter} = 0.001 \text{ liter}$$

The liter was originally defined as 1000 cubic centimeters, but is now defined as the volume of a kilogram of water at maximum density. The standard is slightly greater than 1000 cubic centimeters and is equal to 1000.028 cubic centimeters. This means that one milliliter is equal to 1.000028 cubic centimeters. It is such a close approximation, that chemists sometimes use the terms "milliliter" and "cubic centimeter" interchangeably.

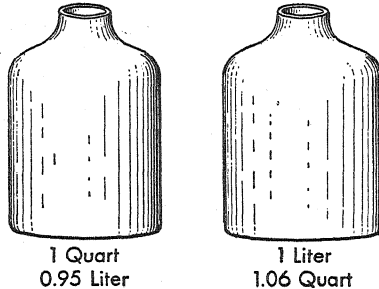


Fig. 3-3.

Metric and English System

1 meter	= 39.37 inches
2.54 centimeters	= 1 inch
1 liter	= 1.057 quarts (liquid)
1 cup	= 0.2366 liter
1 kilogram	= 2.2 pounds
1 ounce (avoirdupois)	= 28.35 grams

Heat

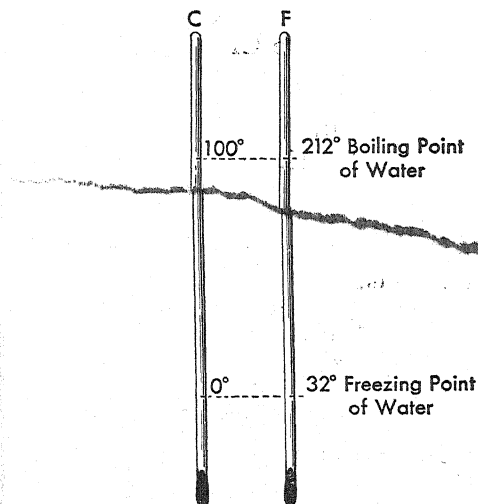
The unit of heat is the calorie. This is equal to the heat necessary to raise the temperature of 1 gram of water 1° centigrade. (Precisely, it is measured from 14.5° to 15.5° C.) The kilogram calorie or large calorie is the unit commonly used in nutrition and medicine. 1 Calorie (kilogram calorie) = 1000 calories.

Temperature

Temperature is commonly measured in the chemical laboratory by means of the centigrade scale. This is a scale on which the freezing point of water at 760 mm. pressure is 0°, and the boiling point at 760 mm. pressure is 100°. Since these points on the Fahrenheit scale, which is commonly used here in the United States, are 32° and 212°, it is a very different kind of scale. The reading on one scale may be converted into a reading on the other scale by a simple calculation:

$$C. = \frac{5}{9}(F. - 32^{\circ})$$

$$F. = \frac{9}{5}C. + 32^{\circ}$$



Centigrade and Fahrenheit
Temperature Scales

Fig. 3-4.

Density and Specific Gravity

The density of a substance is *defined as its weight per unit volume*. Thus the density of, say, iron may be given in terms of grams per cubic centimeter or pounds per cubic inch or foot. It is 7.86 grams/cubic centimeter or 491.25 pounds/cubic foot. This means that exactly one cubic centimeter of iron weighs 7.86 grams. In using density the units used must always be indicated.

The *relative density* of a substance is called its *specific gravity*.

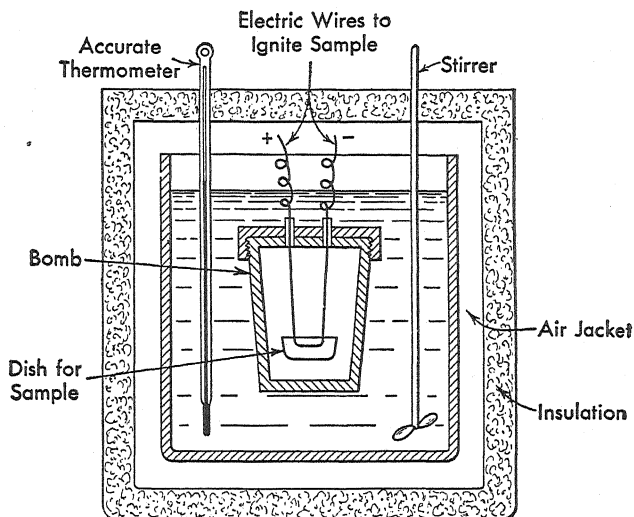


Fig. 3-5. A bomb calorimeter for measuring calories.

Usually the density of a solid or liquid is compared to water at 4° centigrade. Gases may be compared to air, oxygen, or hydrogen. When the reference substance is not given, the specific gravity is the relative density of the substance compared to *water*. For the iron above:

$$\text{Specific gravity} = \frac{\text{Density of iron}}{\text{Density of water at 4° C.}} = \frac{7.86 \text{ g./cc.}}{1 \text{ g./cc.}} = 7.86$$

On the English scale the specific gravity is the same:

$$\text{Specific gravity} = \frac{\text{Density of iron}}{\text{Density of water}} = \frac{491.25 \text{ lb./ft.}^3}{62.5 \text{ lb./ft.}^3} = 7.86$$

Notice, that in specific gravity, units are not used. Specific gravity is a *ratio*, the number of times more dense a substance is than the reference substance.

It is sometimes said loosely that iron is heavier than feathers. Of course it is meant that iron is *denser* than feathers, that if there is an equal volume of iron and of feathers, the iron will be heavier. Or it is said correctly that the specific gravity of iron is higher than that of feathers.

Metric Units*Distance*

- 1 kilometer = 1000 meters
- 1 decimeter = 0.1 meter
- 1 centimeter = 0.01 meter
- 1 millimeter = 0.001 meter

Weight

- 1 kilogram = 1000 grams
- 1 decigram = 0.1 gram
- 1 centigram = 0.01 gram
- 1 milligram = 0.001 gram
- 1 microgram = 0.000001 gram = 0.001 milligram

Volume

- 1 milliliter = 0.001 liter

NEW TERMS

Metric system, meter, kilometer, decimeter, centimeter, millimeter, gram, kilogram, decigram, centigram, milligram, liter, milliliter, calorie, Calorie, centigrade, density, specific gravity.

QUESTIONS

1. What is the advantage of the metric system over the English system of weights and measures?
2. How many meters are in 3 meters, 150 centimeters, and 2 millimeters?
3. Add 5 grams, 51 centigrams, and 15 milligrams.
4. Add 48 grams, 172 centigrams, and 7 milligrams.
5. A pencil is 6 inches long. How many centimeters is it? How many meters?
6. How many liters will a 2-quart stewing pan hold?
7. If you were buying sheets in France and wanted them to be at least 108 inches long, how many meters would they have to be?
8. A window is 4 feet wide and 8 feet tall. How many square meters does it contain?
9. A pair of drapes contains 6 yards of material. How many meters is this?
10. Calculate your body weight in kilograms.
11. A recipe calls for the use of a pound of sugar. How many grams would you use? Kilograms?

12. What is the weight of a teaspoon of water in grams? A quart of water?
13. What is density? What is specific gravity? What is the difference between them?
14. Calculate the density of a piece of wood which weighs 5.18 grams and which has a volume of 6 milliliters.
15. Calculate the specific gravity of a liquid, 15 ml. of which weigh 20.45 grams.
16. A calorimeter holds 2 kilograms of water. When a sample of bread weighing 10 grams is burned in the calorimeter, the temperature of the water rises from 15° to 18° C. How many calories are given off by the bread? How many are present in 1 gram of bread?
17. Calculate the number of small calories necessary to heat 250 grams of water from 5° to 25° C.

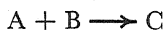
Simple Chemical Reactions

In Chapter 2, it was pointed out that the many changes in matter which are experienced in everyday life are either physical changes or chemical changes. You will remember that chemical changes are changes in the molecular composition of a substance or of some substance in a mixture, and that changes in properties as well as loss or gain of energy indicate, but do not absolutely prove, that a chemical change is taking place. Some of the chemical reactions which are experienced in daily life are single simple reactions as when boiler scale deposits on the bottom of the tea kettle, or when a gas is given off when baking powder reacts. Other events may consist of a complex chain of reactions as when a flower blooms or your muscle contracts. Very simple chemical reactions are easy to understand and will be studied first.

Types of Simple Reactions

When substances react chemically, the composition of one or more molecules change and new molecules with different composition are formed. There are four types of simple chemical reactions.

Combination or Synthesis



An example is the burning of magnesium. Shiny, metallic magnesium burns brightly in air to form a grayish white powder.

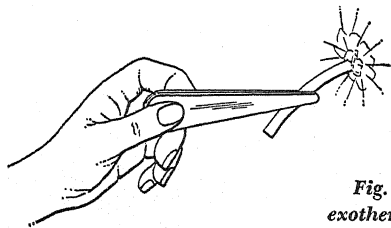


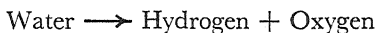
Fig. 4-1. Burning magnesium ribbon, an exothermic reaction.

Magnesium and oxygen of the air combine to form magnesium oxide. Another example is the reaction of zinc and sulfur to form zinc sulfide. When these two elements are heated together, they soon flame and produce a yellow gray powder, zinc sulfide. The products of such reactions are compounds.

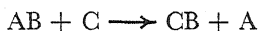
Decomposition or Analysis



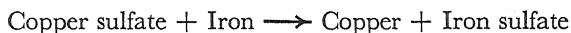
An example of decomposition is the electrolysis of water. When an electric current is passed through a very dilute solution of sulfuric acid in water, the water *decomposes* and forms oxygen and hydrogen gas. One gas collects at one electrode and another at the other electrode. They are both colorless and odorless, but their chemical properties are different.



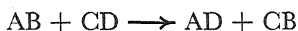
Substitution or Replacement



If an iron nail is dropped in a solution of copper sulfate, the nail soon becomes coated with copper and the blue color of the copper sulfate fades. This is an example of substitution in which the reaction is:



Double Decomposition or Double Replacement



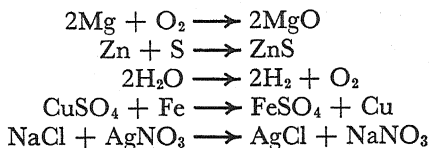
This is a simple type of chemical reaction in which there is an exchange of partners. The positive ion, A, loses its negative ion B, and takes on another negative ion, D. If a solution of sodium chloride is added to a solution of silver nitrate, a white insoluble compound is formed. (An insoluble substance produced by chemical reaction and thrown out of solution is called a *precipitate*.)



Equations

Chemical shorthand, a balanced equation, is used to explain the course of a chemical reaction. An equation shows (1) the

substances which are reacting, (2) the substances which are produced, and (3) the relative quantities of substances which react and which are produced. The equations for the five reactions used as examples in the above section are:

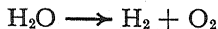


The first equation explains that two molecules of magnesium, each containing one atom to the molecule, reacts with one molecule of oxygen which contains two atoms to the molecule, to produce two molecules of magnesium oxide, each of which contains one atom of magnesium and one atom of oxygen.

The second equation is a little easier. It shows that one molecule of zinc, containing one atom to the molecule, reacts with one molecule of sulfur, which also contains one atom to the molecule, to produce one molecule of zinc sulfide, which contains one atom of zinc and one atom of sulfur to the molecule.

To write chemical equations, the following procedure is observed:

1. Write correct formulas of reactants.
2. Write correct formulas of products.
3. Balance the equation, i.e., make the number of atoms on one side of the equation balance those on the other side. Take as an example the reaction: water yields hydrogen and oxygen. First the formula for the reactant water, H_2O , is written; then the formulas for the products, hydrogen, H_2 , and oxygen, O_2 .

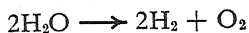


Now the third step in the procedure is to balance the equation. The number of atoms on each side of the equation must be equal since matter is not destroyed nor created. There are in the present equation two atoms of hydrogen in the molecule of water and two atoms of hydrogen in the molecule of hydrogen. They are, therefore, balanced. However, there is only one atom of oxygen on the left-hand side in the molecule of water, and there are two atoms on the right-hand side in the molecule of oxygen. They are not balanced. In order to balance them,

two molecules of water must react. (The composition of water cannot be changed. It is always H_2O with only one atom of oxygen to the molecule.)



The oxygen is now balanced, but the hydrogen is not. There are now four atoms of hydrogen on the left-hand side, and two on the right-hand side. The equation is balanced by writing two molecules of hydrogen, 2H_2 . (Again, the composition of the hydrogen cannot change. It exists with two atoms to one molecule and we are trying to explain in the equation what occurs.)



The equation is balanced.

Laws Governing Chemical Reactions

There are a number of laws which chemical reactions follow, two of which must be recognized immediately. These are the Law of Conservation of Matter and the Law of Definite Proportions. Reference has already been made to each of these laws.

The Law of Conservation of Matter states that matter can neither be destroyed nor created. This, of course, applies to chemical reactions. From our present day knowledge, this seems logical. If exactly 100 grams of material is allowed to react, exactly 100 grams is produced. Matter is not created in a chemical reaction, although the manner in which the elements are combined is affected. It took several centuries of study before this fact became evident in chemistry. Iron rusts and gains weight; wood burns and loses weight. The early investigators were confused since they did not weigh all the reactants in the case of the iron (they omitted the air with which it reacted) or did not weigh all the products in the case of wood (they omitted the gases, carbon dioxide, and water, produced).

The Law of Definite Proportions states that substances react with one another in definite proportions and produce definite amounts of products. Another form of the Law of Definite Proportions has been referred to. It states that compounds have definite composition. This law means that if it is observed that 32 grams of sulfur will react with 32 grams of oxygen, then under

similar conditions the same proportions will always react. In other words, one gram of sulfur will react with one gram of oxygen and 320 grams of sulfur will react with 320 grams of oxygen.

Energy Changes

Chemical reactions are always accompanied by some change in energy. Either, when the reaction occurs, energy is absorbed or energy is produced. The energy may be light, kinetic energy of motion, electricity, or most commonly, heat or a combination of these forms of energy. Reactions are classified according to this change in energy either as *exothermic* or *endothermic* reactions. *An exothermic reaction is a chemical reaction in which energy is released.*

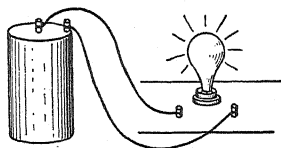
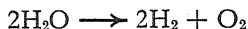


Fig. 4-2. Drawing current from a dry cell, an exothermic reaction.

An endothermic reaction is a chemical reaction in which energy is absorbed. When anything burns — wood, gasoline, magnesium — an exothermic reaction occurs. When an explosion occurs, or when electricity is withdrawn from a battery, these are exothermic reactions. Examples of endothermic reactions are the decomposition of water which occurs when electricity passes through it, the formation of carbohydrates in a leaf when sunlight falls on it and photosynthesis occurs, the recharging of a battery, and the exposure of a photographic film to light.

Weight-Weight Relations

Since chemical compounds react in definite proportions, it is possible to calculate the amount of a substance which will react with a definite amount of another substance, or the amount of product which will be formed. The balanced equation not only shows the ratio of molecules by which compounds react, but also the ratio of grams, or any other units of weight. There are the same number of molecules in one gram molecular weight of any substance, namely 6.02×10^{23} molecules (Avogadro's number). Thus the equation means:



2 molecules produce 2 molecules + 1 molecule

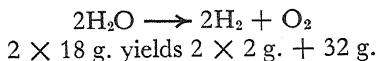
or $2 \times 6.02 \times 10^{23}$ molecules produce $2 \times 6.02 \times 10^{23}$ molecules + 6.02×10^{23} molecules

or 2 gram molecular weights produce 2 grams molecular weights + 1 gram molecular weight

Pound molecular weights or ton molecular weights or any other units which are convenient may be used. The gram molecular weight of a substance is its molecular weight expressed in grams, or it is the sum of the atomic weights of each atom in the molecule expressed in grams. The gram molecular weight of water, H_2O , is: 2 (1 for each hydrogen) + 16 (for oxygen) = 18. The equation shows that 2×18 grams of water produces 2×2 grams of hydrogen and 32 grams of oxygen, and it is known from the Law of Definite Proportions that water will always decompose in *this ratio*. Therefore, the quantities of reactants or products under other conditions can readily be calculated.

EXAMPLE: How many grams of oxygen and hydrogen will be produced by the electrolysis of 9 grams of water?

ANSWER: The balanced equation shows the ratio of grams of reactant and products. These are written below each formula in the equation.



Now compare the amount of water given in this particular equation to the amount which the equation shows, 2×18 g. and the amount of hydrogen, X , with the amount which the equation predicts will be produced from 2×18 g. of water. This will give:

$$\frac{9 \text{ g. H}_2\text{O}}{2 \times 18 \text{ g.}} = \frac{X \text{ g. H}_2}{2 \times 2 \text{ g.}} \quad X = 1 \text{ g. hydrogen}$$

Likewise in solving for the amount of oxygen which will be formed, compare the given amount of water to 2×18 g., as the unknown amount of oxygen, Y , is to 32 g.

$$\frac{9 \text{ g. H}_2\text{O}}{2 \times 18 \text{ g.}} = \frac{Y \text{ g. O}_2}{32 \text{ g.}} \quad Y = 8 \text{ g. oxygen}$$

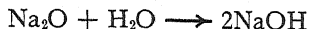
In calculating weight-weight problems, write the *balanced equation* first and then set up the proportion and solve for the unknown.

NEW TERMS

Equation, balancing, exothermic reaction, endothermic reaction.

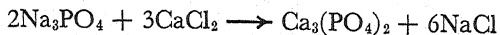
QUESTIONS

- Balance the following equations:
 - $\text{CuCl}_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CuCO}_3 + \text{NaCl}$
 - $\text{SO}_2 + \text{O}_2 \longrightarrow \text{SO}_3$
 - $\text{Cu} + \text{S} \longrightarrow \text{Cu}_2\text{S}$
 - $\text{H}_2\text{O} \longrightarrow \text{H}_2 + \text{O}_2$
 - $\text{NaC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{HC}_2\text{H}_3\text{O}_2$
 - $\text{Fe}(\text{NO}_3)_3 + \text{NH}_4\text{OH} \longrightarrow \text{Fe}(\text{OH})_3 + \text{NH}_4\text{NO}_3$
 - $\text{AgNO}_3 + \text{MgCl}_2 \longrightarrow \text{AgCl} + \text{Mg}(\text{NO}_3)_2$
 - $\text{Al}(\text{OH})_3 + \text{HBr} \longrightarrow \text{AlBr}_3 + \text{H}_2\text{O}$
 - $\text{Ca} + \text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2$
- How does the Law of Conservation of Matter apply to chemical reactions? Explain.
- How does the Law of Conservation of Energy apply to chemical reactions? Explain.
- Complete and balance the following double decomposition reactions:
 - $\text{NH}_4\text{OH} + \text{H}_2\text{SO}_4$
 - $\text{BaCl}_2 + \text{K}_2\text{CO}_3$
 - $\text{Ca}(\text{NO}_3)_2 + \text{H}_2\text{SO}_4$
 - $\text{FeCl}_2 + \text{H}_2\text{S}$
 - $\text{NaOH} + \text{H}_3\text{PO}_4$
 - $\text{AgNO}_3 + \text{KBr}$
 - $\text{Ca}(\text{OH})_2 + \text{HCl}$
 - $\text{ZnCl}_2 + \text{NH}_4\text{OH}$
- Fifteen grams of sodium oxide is added to water, where it reacts to form sodium hydroxide according to the following equation:



Calculate the number of grams of water which react. How much sodium hydroxide is produced?

- Sodium phosphate reacts with calcium chloride according to the following equation:



Calculate the amount of sodium phosphate which will react with 22 grams of calcium chloride.

7. How much hydrogen will be produced from the reaction of 1 gram of zinc with hydrochloric acid?



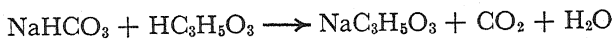
What weight of hydrochloric acid will react? How much zinc chloride will be formed?

8. Sulfur reacts with oxygen to form sulfur dioxide. How much oxygen will react with 3.2 grams of sulfur?



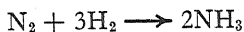
What weight of sulfur dioxide will form?

9. Baking soda (NaHCO_3) reacts with the lactic acid of sour milk to form carbon dioxide.



What weight of baking soda will react with 1 gram of lactic acid?

10. Nitrogen and hydrogen react to form ammonia according to the following reaction:

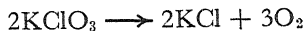


How much nitrogen will react with 2 grams of hydrogen? What weight of ammonia will form?

11. In order to prepare 50 grams of cupric sulfide in the laboratory from the action of cupric sulfate and hydrogen sulfide, how much cupric sulfate must be used?



12. Exactly 1 gram of oxygen is needed in the laboratory and it can be readily prepared by decomposing potassium chlorate.



How much potassium chlorate is required?

Oxygen

The properties of matter in general have been briefly studied. Now the application of these laws and theories to the chemistry of one element, oxygen, will be discussed. Oxygen is the first element studied because of its abundance in our environment and its importance in daily life. It is present as one of the elements in many of the compounds which make up the soil, clothing, plants, and animals, and many other substances in our environment, and it is present as a free element in the air.

The air in which man lives is a gaseous envelope, surrounding the earth, with its greatest density at sea level. It is composed of a mixture of gases, nitrogen, carbon dioxide, water, rare gases, and *oxygen*. The oxygen makes up approximately one-fifth of the volume of the air or approximately 25 per cent of the weight. The oxygen present in the air is absolutely essential for our life.

Occurrence

When the occurrence of a gaseous element is discussed and the percentage of that element in gaseous mixtures, in liquids, and in solids is given, it is necessary to indicate whether the percentage is expressed in terms of volumes or of weights. The reason for this lies in the fact that they are usually different. Avogadro showed that equal volumes of gases contain the same number of molecules. One liter of oxygen at 0° C. and 760 mm. pressure will have the same number of molecules as 1 liter of nitrogen measured under the same conditions. But the weights of these volumes will be different since each oxygen molecule weighs 32 while each nitrogen molecule weighs 28. One liter of oxygen at 0° C. and 760 mm. pressure weighs 1.4290 grams, while 1 liter of nitrogen weighs 1.2507 grams. If these two 1 liter volumes are mixed, they will produce a volume of 2 liters which is 50% oxygen and 50% nitrogen by volume. The weight will be 2.6797 grams, of which 1.4290 grams will be oxygen and

1.2507 grams will be nitrogen. The mixture will, therefore, be 53.3% oxygen by weight.

The earth's crust is composed of compounds which contain oxygen. It is a complex mixture of compounds varying considerably in its composition from one locality to another. In general the amount of oxygen in this mixture of compounds is approximately 50% oxygen by weight. Your body is composed of water, carbohydrates, lipids, proteins, salts such as calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, and many other substances present in small amounts. All these compounds contain oxygen. The average amount of oxygen in your body is between 60 and 65 per cent depending on how fat or slim you are.

History

The presence of free oxygen in the atmosphere and, indeed, the occurrence of the element were not recognized until the time of the American Revolution. Some alchemists and early chemists appear to have observed that there was something in air essential for life and for burning, but they never carefully identified it or gave it the status of an element. This neglect, despite the abundance of oxygen, resulted from the prominence of an erroneous theory of combustion. In 1669, Becher offered the Phlogiston Theory of Combustion, a theory which was used for 140 years. This theory explained combustion as a process in which a substance lost "phlogiston." He was exactly wrong for it is known now that combustion is a process in which a substance combines with oxygen. Priestley is given credit for

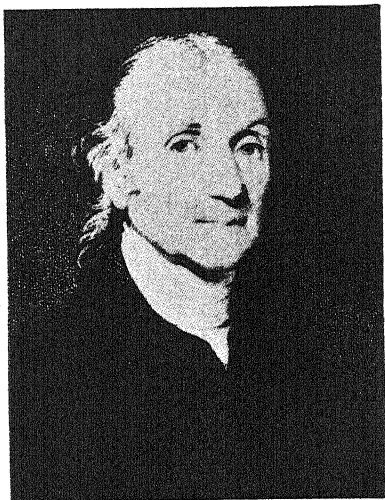


Fig. 5-1. Joseph Priestley. (Courtesy of Journal of Chemical Education.)

the discovery of oxygen in 1774. It has been shown that a Swedish chemist, Scheele, actually prepared the gas before this time, but his work was not published until after Priestley's. At the time of the discovery, Priestley was attempting to prepare gases by heating almost anything he could find, with a "burning lens" (a magnifying glass), and collecting any gas which was evolved. One of the substances which he heated was mercuric oxide. This readily decomposes to form mercury and oxygen. Priestley collected the oxygen and observed that a candle burned brightly

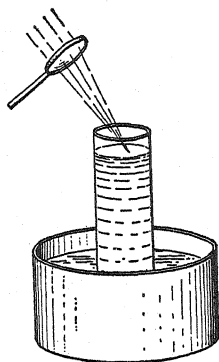


Fig. 5-2. Diagram of Priestley's apparatus. Red mercuric oxide was floated on top of mercury in an inverted cylinder in a well of mercury. Priestley heated the mercuric oxide by focusing the sun's rays on it. He knew a gas was given off since the level of the mercury in the cylinder fell.

in the gas and that mice were able to live in it. He thought this was interesting but apparently he did not recognize the full importance of his discovery. (In 1794, as an old man, Priestley left England and moved to Pennsylvania, where he lived for the last ten years of life. Some of his laboratory equipment is owned by Dickinson College and may be seen in its museum.)

The brilliant French chemist, Lavoisier, was working along similar lines. He made numerous observations on this gas and showed, for example, that oxygen exists in ordinary air and to the extent of about 20 per cent by volume. He concluded, erroneously, that all acids contained this element and he, therefore, named it "oxygen" from the Greek for "acid former." In 1772 Lavoisier had started on the trail of the correct theory of combustion and Priestley's discovery of oxygen hastened its complete substantiation. Although Lavoisier presented excellent work to support his theory of combustion, Priestley was never convinced and until his death in 1804 argued for the Phlogiston Theory.

Properties

Oxygen is an odorless, tasteless, and colorless gas at room temperature. It does affect the flavor of water when it is dissolved in the water. Boiled water from which all the oxygen has been driven has a flat taste. The solubility of oxygen in water is limited, diminishing with an increase in temperature.

Solubility of Oxygen at Standard Pressure

<i>Temperature</i>	<i>Volume in one volume of water</i>
0° C.	0.04889
20	0.03102
50	0.02090
80	0.01761
100	0.00000

You are familiar too with evidences of this decreased solubility for you have all observed bubbles of air containing oxygen deposited on the sides of a glass as water in the glass warms to room temperature. Fish sometimes die in small shallow ponds

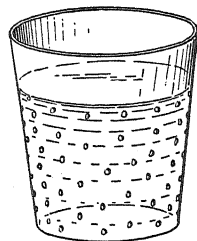
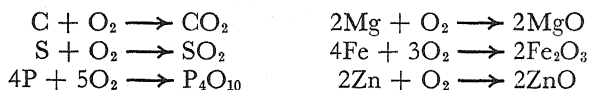


Fig. 5-3. Air bubbles form on the side of a glass as water warms to room temperature and the solubility of air decreases.

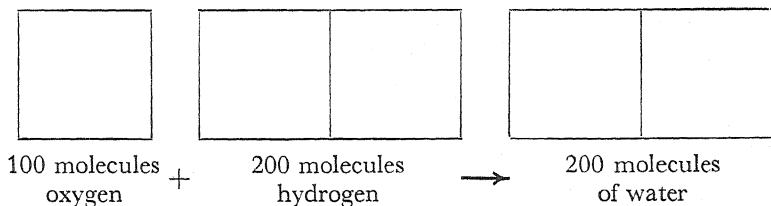
during very hot weather when the temperature of the water in these small-volume ponds rises above normal summer temperatures. If oxygen gas is cooled and compressed, it condenses to a blue liquid with the low boiling point of -183°C . at 760 millimeters of pressure.

Chemically, oxygen is a very active element. The term "active" means that the element combines readily with a great many substances. An element is called "stable" or "inactive" if it combines with only a few elements and then only at high temperatures or high pressures. An element is called "inert" if it does not combine with anything. Oxygen combines with

both metals and nonmetals. The elements may be divided into three categories, the metals, the nonmetals, and the inert elements. The metals have the physical properties which are commonly associated with the term "metal" — luster, malleability, ductility, as well as certain chemical properties. The common chemical properties will be discussed later. For the present, the idea which you have of "metal" may be used to differentiate these elements from nonmetals. Some metals with which you are familiar are gold, silver, chromium, platinum, zinc, lead, iron. Nonmetals are elements which do not have the physical properties of metals and which have some chemical properties in common. The ones which you probably know are carbon, sulfur, chlorine, and iodine. The inert elements are those which do not react chemically and which therefore do not have any chemical properties. They are helium, neon, argon, krypton, xenon, and radon. Oxygen combines with all metals and nonmetals except platinum, gold, iodine, bromine, and fluorine and it will combine with compounds of these elements. Examples are found in the following reactions:



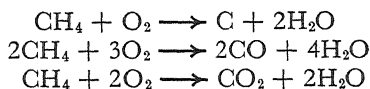
A molecule of the free element, oxygen, is composed of two atoms, and the formula is written O_2 . One line of evidence in support of this comes from careful observations of the volumes of oxygen and hydrogen which react and the volume of gaseous water produced. Whenever oxygen and hydrogen combine, the *ratio* of their volumes when they are measured at the same temperature and pressure, is one to two. Thus 1 milliliter of oxygen combines with 2 of hydrogen, or 100 milliliters of oxygen combine with 200 of hydrogen. The volume of water vapor, measured as a gas, is equal to twice the volume of oxygen. Since equal volumes of gases, measured under the same conditions, contain the same number of molecules, one volume of oxygen contains half the number of molecules as two volumes of hydrogen or as two volumes of water vapor. To use simple numbers, 100 molecules of oxygen contained in one volume exactly react with 200 molecules of hydrogen in two volumes to form 200 molecules of water in two volumes.



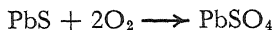
Now if each molecule of water contains just one atom of oxygen, the 200 molecules will have a total of 200 atoms of oxygen. Since these 200 atoms of oxygen originated in 100 molecules of oxygen which reacted, there were two atoms of oxygen in each molecule.

Further proof for the deduction that oxygen contains two atoms in each molecule comes from the determination of the gram molecular weight. The methods of determining gram molecular weights will be given later. These methods measure the approximate gram molecular weight of a substance and, when they are applied to oxygen, the gram molecular weight is found to be 32 grams. Since the atomic weight of oxygen is 16, there must be two atoms in each molecule.

Compounds also sometimes react with oxygen. Examples of this are found in the burning of methane where the nature of the products depends on the amount of oxygen available for the reaction.



Occasionally oxygen will combine directly with a compound:



Many of the reactions of oxygen and other elements or compounds are markedly exothermic reactions where much heat and light are given off. *Any reaction which gives off heat and light is called "burning" or "combustion."* In daily life, combustion or burning is usually the result of the reaction of oxygen and some other substance. This need not be true, however, since other reactions show this same phenomenon. You will see in the laboratory the combination of chlorine and iron in which the iron *burns* in the chlorine. When burning takes place, the gas which is part of the reaction, is said to *support combustion*. Thus when methane burns in air, the oxygen of the air *supports* this

combustion. When iron burns in chlorine, the chlorine supports combustion. Many substances combine slowly with oxygen at room temperature with the slow evolution of heat. The heat is readily dispersed and it is not usually evident that it is being evolved. Thus magnesium ribbon in a bottle on the shelf in the laboratory slowly loses its shiny appearance and becomes coated with the white powdery material which can be identified as magnesium oxide. However, if the magnesium is warmed by heating, it will flame and *burn*. Actually the same reaction is occurring in the laboratory, but at such a slow rate that there is no light evolved and the heat is dissipated. If the magnesium is slowly warmed, there is one temperature at which and above which burning occurs. This is called the *kindling temperature*. *The kindling temperature is the temperature above which a substance burns.* Occasionally substances are protected from the dissipation of the heat formed by these slow reactions. The temperature of the substance will slowly rise and the production of heat will occur faster and faster, until the kindling temperature is reached. Then the substance will burst into flames. This is called *spontaneous combustion*. Oily rags stored in a closed box will sometimes ignite spontaneously. Wet hay stored in a barn will undergo bacterial decomposition. These bacteria produce heat just as man does and the temperature of the hay will rise until it may reach the kindling temperature.

The term "oxidation" is applied to all these reactions of oxygen. *An oxidation reaction is one in which there is an increase in positive valence of one element.* When oxygen combines directly with other elements, these elements gain in valence. A free element has a zero valence since it is not combined with anything. There are also other reactions which are *oxidation reactions*, in which oxygen is not a reactant. Any reaction in which there is a gain of positive valence by an element is called oxidation.

Rate of Reaction

The rate of reaction is the speed at which a reaction occurs. It may be measured, for example, in terms of grams of a product formed in one minute. The rates of all reactions are influenced by three conditions:

1. Temperature. Increases in temperature speed up a reaction. A very rough generalization is that the rate doubles

for every 10° centigrade rise in temperature. This would mean that if 1 gram of product were formed per minute for a reaction carried out at 20°, 2 grams would be formed per minute at 30°, and 4 grams per minute at 40°.

2. Effective concentration of reactants. An increase in the concentration of a reactant accelerates the reaction.

3. Catalysis. Catalysis is a phenomenon in which a substance (the catalyst) influences the speed of reaction, but is itself unchanged in concentration by the reaction. Positive catalysts cause an *increase* in the speed of the reaction, while negative catalysts cause a *decrease*. Some catalysts appear to have the ability to inaugurate a reaction. This is particularly true of biological catalysts (enzymes) although it is not confined to them.

There are many examples of the influence of these three conditions on reaction velocity in the reactions of oxygen. Thus in order to make wood burn rapidly it is necessary to warm it up by burning paper around it. You also observed that magnesium reacts rapidly with oxygen when its temperature has been increased by warming it in a flame. The effect of concentration may be observed when a comparison is made of the rates of reaction of excelsior and a log. The surface, the effective concentration, is very much increased in the excelsior and it burns much more rapidly than the log. Then too if a match is burned in pure oxygen it flames more vigorously than in air where the concentration of oxygen is lower. The effect of catalysts is demonstrated in the preparation of small quantities of oxygen in the laboratory from potassium chlorate in the presence of manganese dioxide.

Extinguishing Fires

When it is necessary to extinguish a fire, one of two procedures or a combination of them is followed. Either the amount of oxygen available is cut down or the burning mass is cooled below its kindling temperature. When a fire is smothered with a blanket, the supply of oxygen is diminished. When a fire is put out with water, the oxygen supply is cut off by covering the burning material with liquid or steam and it is cooled as well. Water is outstanding in the number of calories necessary to raise its temperature appreciably (1 calorie per gram for each 1° C.). Other liquids used in fighting fire cover the material and exclude

oxygen. With burning oil or fat, water is not only useless but often spreads the fire. If water is poured into burning fat, the fat spatters and floats on the water. The easiest way to extinguish a pan of burning fat in the home is to cover it with a lid, so that oxygen is excluded. In oil fires of considerable size, carbon dioxide gas or carbon dioxide foam is often used. These remain on top of the oil and thereby extinguish the fire.

Preparation

There are a number of general methods for preparing oxygen, some of them commercial methods involving extensive equip-

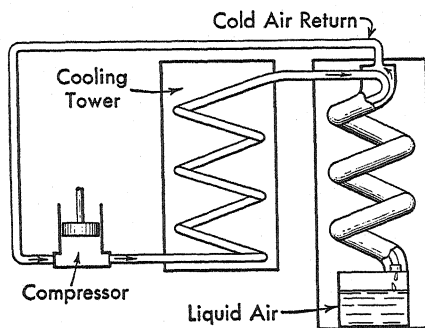


Fig. 5-4. Liquefaction of air. Dry air is compressed and passed through a cooling tower. The temperature is lowered farther by cooling it with return cold air. The liquid air drips into a collecting chamber through a valve, while that which has escaped liquefaction returns to the compressor.

ment and some of them applicable to the preparation of small quantities of oxygen in the laboratory.

1. *From air.* Oxygen occurs free in air and may be separated from the other gases present by distillation of liquid air. Air is dried by passing it over some drying agent which combines with the water in it. The CO_2 and organic materials, such as dust and microorganisms, are removed and the air is compressed to 200 atmospheres pressure (200 times the average pressure at sea level). Cooling of the air under this high compression results in its transformation to a liquid. Liquid air is primarily a mixture of nitrogen and oxygen with small amounts of the rare gases (helium, argon, neon). The boiling point of nitrogen is -195.8°C . and of oxygen is -183°C . Consequently when the liquid air is allowed to warm, the nitrogen boils off (changes back to a gas) first, and the remaining liquid becomes richer and richer in oxygen. By refractionating the oxygen fraction several times, it is possible to produce oxygen of high purity.

Commercially there is little need for oxygen which is absolutely pure. Most of that on the market today is produced from liquid air by a single fractionation and is not absolutely pure oxygen.

2. *From water.* Water is decomposed when an electric current is passed through a dilute sulfuric acid solution. Oxygen bubbles off at the anode (the positive electrode) and hydrogen at the cathode (the negative electrode). The electrodes are composed of some nonreactive material such as platinum. The sulfuric acid does not disappear, but more water must be added from time to time as it is used up. The apparatus must be arranged in such a way that the hydrogen and oxygen are collected separately. This is an endothermic reaction in which electricity is the energy used.

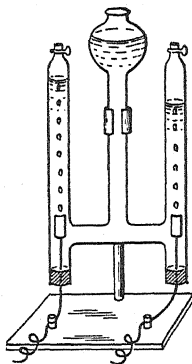
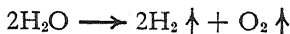
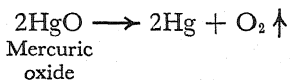


Fig. 5-5. Electrolysis of water. When an electric current is passed through a dilute solution of sulfuric acid, oxygen forms at one electrode and hydrogen at the other. In this apparatus the two gases are trapped in separate compartments. The volume of oxygen formed is just half the volume of hydrogen.

This method is not used extensively in the United States for the production of oxygen, since electricity is relatively expensive.

3. *Decomposition of some compounds.* Some compounds which contain oxygen may be readily decomposed in the laboratory, to produce oxygen although this is by no means a general reaction.

a. Mercuric oxide was used by Priestley in the experiments by which he discovered oxygen. Mercury and mercury compounds are expensive, so that the method is seldom used for producing oxygen in even small quantities.



b. Potassium chlorate is the substance which is most commonly used in the laboratory for the preparation of small quantities of

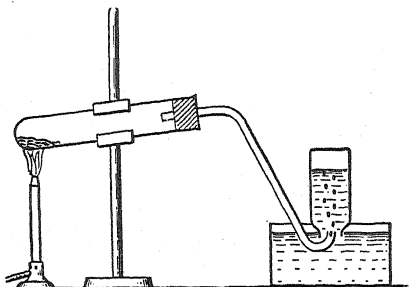
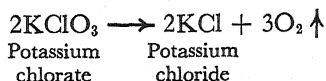


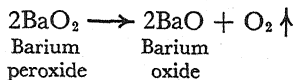
Fig. 5-6. Laboratory preparation of oxygen from potassium chlorate.

oxygen. It decomposes to form oxygen and potassium chloride when it is heated:

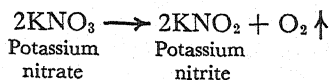
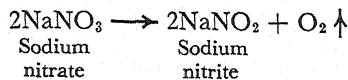


This reaction is accelerated by the presence of MnO_2 or other oxides (ferric, nickel, copper, cobalt), so that decomposition starts at a much lower temperature and proceeds more rapidly. Potassium chlorate, alone, does not begin to decompose until 340°C ., but if it is mixed with manganese dioxide it will decompose at 200°C . This is a curious effect since the manganese dioxide may be recovered unchanged from the reaction mixture. It is the phenomenon known as "catalysis," and manganese dioxide is a positive catalyst.

c. Barium peroxide and sodium and potassium nitrate may be decomposed, if they are heated strongly. The barium peroxide produces barium oxide and oxygen:

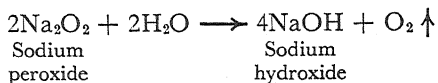


while the nitrates decompose to form nitrites



This is not a general reaction for nitrates, since most decompose to form oxides, nitrogen dioxide, NO_2 , and oxygen.

d. Sodium peroxide will evolve oxygen when it is treated with water.



Oxygen and Life

Most animals show a need for a continuous source of molecular oxygen. The few exceptions are the anaerobic ("without air") bacteria, such as the organisms which cause botulism, anthrax, or tetanus. These organisms do not use oxygen. In man air is breathed into the lungs. Most of the inspired breath remains in the bronchi, the "tree and branches" of the respiratory system, while small amounts are drawn into the alveoli, the tiny sac-like structures of the lung. In the alveoli, a very thin membrane separates the gases in the sac from the blood in the capillaries and an exchange of gases takes place. Some oxygen is absorbed and some carbon dioxide is released. The expired air is 4 to 5 per cent poorer in oxygen and 3 to 4 per cent richer in carbon dioxide. The oxygen absorbed by the blood reacts with the red pigment, hemoglobin, present

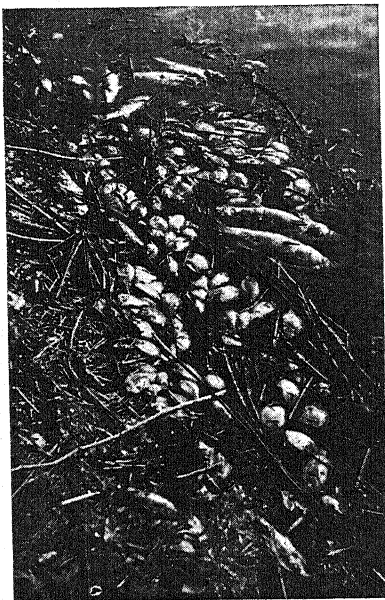
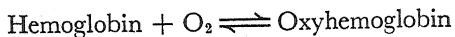


Fig. 5-7. Typical section of the shore line following the melting of ice. Thousands of bass, perch, bluegills, and other fish died because of a severe oxygen deficiency. When heavy snow covers the ice and shuts off sunlight, photosynthesis by tiny plants, planktons, and the consequent formation of oxygen stops. (Courtesy of Michigan Department of Conservation Institute of Fisheries Research.)

in the red blood cells, to form oxyhemoglobin, a very bright red pigment.



This reaction is an *equilibrium reaction*, a reaction in which there is always some reactant and some product present, one which does not go to completion. The amount of oxyhemoglobin formed depends on the concentration of the hemoglobin as well as the concentration of the oxygen. A double arrow indicates an equilibrium reaction.

The blood carries the oxyhemoglobin to the tissues where oxygen is released for cell oxidations by the reaction of the oxyhemoglobin with other compounds. The exact reactions are not known, but bubbles of molecular oxygen are *not* produced at the tissue. The reaction is probably:

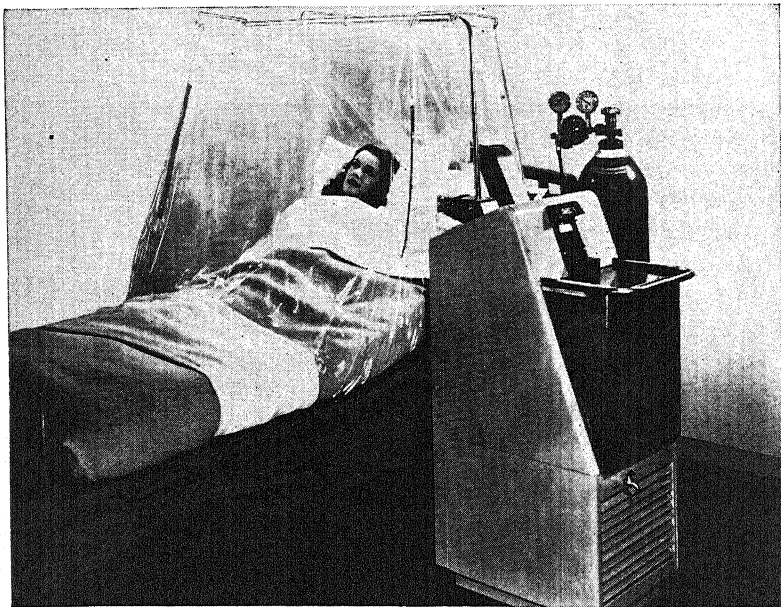
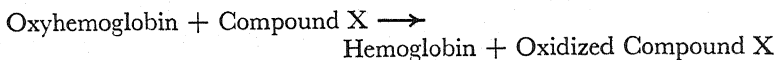


Fig. 5-8. An oxygen tent. In an oxygen tent the mixture of oxygen and air is recirculated. This oxygen tent is provided with an air cooling device; others warm the air. The physician prescribes the concentration of oxygen to be used in the tent. (Courtesy of the Linde Air Products Company.)

Hemoglobin is carried by the blood back to the lungs where it again reacts with oxygen.

Uses

Oxygen is used in medicine whenever it is desirable to increase the concentration of oxygen in order that the quantity of oxyhemoglobin formed at the lung may be increased. Oxygen tents may be seen in almost any hospital. In cases of carbon monoxide poisoning the quantity of hemoglobin may be reduced to dangerously, even fatally, low levels by the combination of the carbon monoxide with the hemoglobin. Oxyhemoglobin cannot then be formed in normal amounts. Oxygen-enriched air or even commercial oxygen may be administered to these patients. In any kind of asphyxia, the quantity of oxygen may be increased. When the circulation of the blood is impaired in a circulatory or cardiac failure or when the amount of blood coming in contact with air is subnormal as in pneumonia where one or both lungs may fill with fluid, oxygen is used to increase the amount of oxyhemoglobin produced.

Oxygen is also used in high-altitude aviation. In small planes, oxygen masks may be used by the crew in order to maintain normal concentrations of oxygen. This is not completely satisfactory. High-altitude flying presents two physiological problems: (1) the low concentration of gases inhaled, particularly oxygen, and (2) since the air is "thin," the low pressure of the air

Fig. 5-9. A nasal face mask for administering oxygen. A mixture of oxygen and air flows into the breathing bag which expands and collapses as the patient breathes. The quantity of oxygen depends on the patient's condition and is prescribed by the physician. The patient must breathe through his nose, but can eat or take medicine without removing the mask. Another type of mask covers both the nose and mouth. (Courtesy of the Linde Air Products Company.)



which diminishes the solubility of all gases in the blood, sometimes causing the formation of bubbles in the blood stream. The concentration of oxygen may be increased by a face mask, but this device will not prevent bubble formation in the blood vessels. An air or nitrogen bubble is usually very painful and may be very dangerous. If it occurs in some strategic blood vessel such as an artery to the heart or brain, it may block that vessel and cause death. In larger aircraft it is possible to seal the cabin and maintain higher pressures and therefore high concentrations of the atmospheric gases. During World War II experiments were made with pressure suits in which the aviator was surrounded by an atmosphere similar to that of the earth's surface. The chief objection was the clumsiness of these bulky suits.

Oxygen is also used in producing very hot flames for welding or for cutting metals. When the concentration of oxygen is increased in an exothermic reaction, the speed of the reaction increases and also the amount of heat produced in a unit time. An extremely hot flame may therefore result. Torches are used which consume acetylene (oxyacetylene blow torches), hydrogen (oxyhydrogen torches), and hydrocarbon mixtures.

Oxides

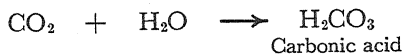
An oxide is a binary compound containing



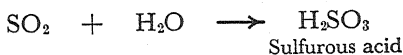
Fig. 5-10. An oxyacetylene welding blowpipe. The worker is welding a cracked steel plough wheel. Welding and cutting is a fast and easy way to repair things made from metal. (Courtesy of the Linde Air Products Company.)

oxygen and another element. The oxides of metals which react with water (not all oxides do react with water) produce a base. The oxides of nonmetals which react with water produce an acid.

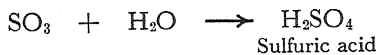
An acid is a substance with a sour taste which neutralizes bases and which has a definite effect on certain dyes (indicators). Chemically an acid is a compound which produces hydrogen ions. Some acids are formed by the reaction of a nonmetallic oxide with water, others may be formed by different types of reactions.



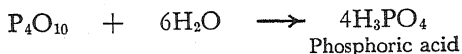
Carbonic acid



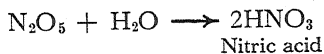
Sulfurous acid



Sulfuric acid



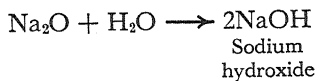
Phosphoric acid



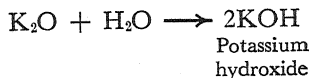
Nitric acid

A nonmetallic oxide is sometimes called an *acid anhydride* (literally an acid without water).

A base is a substance which has a bitter taste and soapy feel — it neutralizes acids — and has a definite effect on certain dyes (indicators). Chemically several types of compounds have these properties. At present, the term “bases” will refer only to those compounds which produce an hydroxyl ion (OH). These may be called *hydroxides*. The term “alkali” is also applied to a large group of compounds having properties of bases, whether or not they produce hydroxyl ions. It is not used as precisely as the term “hydroxide.” Hydroxides or bases may be formed by the reaction of water with a metallic oxide.



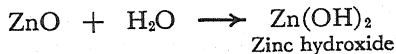
Sodium
hydroxide



Potassium
hydroxide



Calcium hydroxide



Zinc hydroxide

NEW TERMS

Active element, stable element, metal, nonmetal, burning, combustion, kindling temperature, spontaneous combustion, oxidation, catalyst, rate of reaction, electrolysis.

QUESTIONS

1. Where does oxygen occur in our environment? Indicate where it is present as the free element or in compounds.
2. Give three reasons why oxygen is important in our everyday life.
3. How can oxygen be removed from water?
4. Give two methods for preparing oxygen in the laboratory.
5. Why is a glowing splint used to test for oxygen?
6. What is the difference between "the ability to support combustion" and "combustible"?
7. Explain how oxygen is produced commercially.
8. How can we prove that MnO_2 is a catalyst for the decomposition of KClO_3 and that it does not lose oxygen at the temperature of the reaction?
9. Why is it not possible to decompose water into oxygen and hydrogen by boiling it?
10. Explain how oxygen is carried to the tissues of the body.
11. Why does a splinter ignite from the heat of a match while a log does not?
12. Why does pouring water on a wood fire extinguish it?
13. Why does pouring water on an oil fire spread it?
14. Why is it dangerous to store oily rags in a small wooden box?
15. Why does the amount of oxygen in the air not decrease when it is such an active element?
16. Why is the formula for a molecule of oxygen written O_2 ?
17. Why is it possible to burn coal but not ashes?
18. Write and balance equations for the reaction of oxygen with (a) sulfur, (b) copper, (c) sodium, (d) phosphorus, (e) silver, (f) zinc, (g) calcium, (h) aluminum. Write the equation for the reaction of each of the oxides which react with water.
19. Calculate the amount of air which must be processed in order to produce 1 kilogram of oxygen. Assume that the process is 100 per cent efficient.
20. Calculate the amount of oxygen which can be formed by the electrolysis of 180 grams of water. How much hydrogen will be formed?
21. How many grams of potassium will combine with 64 grams of oxygen?
22. List some of the uses of oxygen and explain why it is effective.

Hydrogen

Hydrogen is the lightest element. It is present in many compounds and has unusual and interesting properties. It will be studied now because of this significance in compounds.

Occurrence

Hydrogen occurs free in nature in relatively small concentration. It is present in the outer atmosphere to a limited extent and in volcanic gases. Combined hydrogen is common in a great many compounds which are important to us. It is present in water, the most abundant compound, to the extent of 11.1 per cent by weight and it is in most organic compounds. The hydrogen ion is the ion which gives acids their common properties.

History

Hydrogen was known in alchemical times since it may be prepared by the action of iron and acid. It was recognized to be a gas of low density and highly explosive, but it was confused with other gases that have similar properties. In 1766 Cavendish recognized it as a distinct substance, and a short time later Lavoisier gave it the name "hydrogen" or "water-former."

Properties

Hydrogen is a colorless, odorless gas with a very low density, 0.08987 gram per liter at 0° C. and

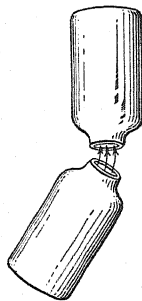
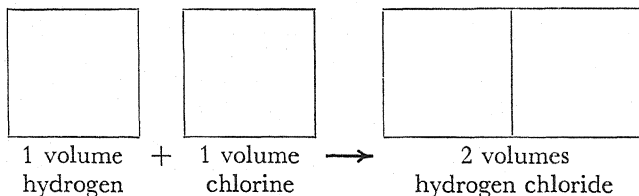


Fig. 6-1. Pouring hydrogen up.

760 millimeters pressure. Since the density of air under the same conditions is 1.2931 grams per liter, the hydrogen is much lighter than air and shows great buoyancy. It may be poured *up* into a cylinder of air, displacing the air. It is difficultly soluble in water. When hydrogen gas is compressed below -241°C . it is changed into a clear, colorless liquid with a boiling point of -242°C . Above this temperature, -241°C ., it exists as a gas at all pressures. Hydrogen is not poisonous although an animal placed in it will die for want of oxygen.

Hydrogen occurs in molecules which contain two atoms to each molecule, H_2 . This is demonstrated in a manner similar to the evidence for the occurrence of two atoms of oxygen per molecule. Hydrogen and chlorine react in equal volumes to produce two volumes of hydrogen chloride:

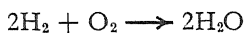


You will remember that equal volumes of gases under the same conditions of temperature and pressure contain equal numbers of molecules. If the volume of hydrogen contains 100 molecules, then there must be 100 molecules of chlorine and 200 molecules of hydrogen chloride. Hence, if each molecule of hydrogen chloride contains one hydrogen atom, there is a total of 200 hydrogen atoms in 100 molecules, or two atoms per molecule.

The chemical properties of hydrogen are demonstrated by the following:

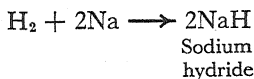
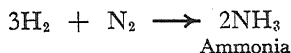
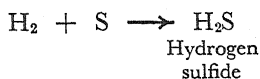
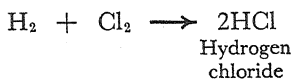
1. Hydrogen will burn in air or oxygen with a pale blue flame. That it will not support combustion is demonstrated by the extinction of a glowing splinter in the pure gas. It forms an explosive mixture with oxygen and air over a wide range and, because of this, great care must be used in its preparation in the laboratory. No large quantities of the gas must ever be collected unless the student is positive that the apparatus is free of air. This can be tested by collecting small quantities in a test tube and igniting the gases. A mixture of hydrogen and air gives an

explosive pop while pure hydrogen will burn quietly at the mouth of the tube, and then on down into the tube. Steam collects on the sides of the test tube in either experiment.

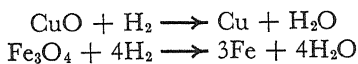


The explosive range of hydrogen and air varies from 9 to 65 volume per cent of hydrogen. This means that mixtures of hydrogen and air from concentrations of 9 volumes hydrogen: 91 volumes air up to 65 volumes hydrogen: 35 volumes air, explode.

2. Hydrogen will combine with some nonmetals and metals to form hydrides.



3. Hydrogen will also react with some compounds. It reacts with some oxides to cause *reduction*. A *reduction* is a chemical reaction in which there is a loss of positive valence by one element.

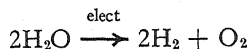


In the first reaction the valence of copper changes during the reaction from plus two to zero. The copper is said to be *reduced*; hydrogen is called the *reducing agent*. You will notice that this reaction is also an oxidation reaction since the valence of hydrogen increases from zero to plus one. The hydrogen is *oxidized* and copper oxide is the *oxidizing agent*. This is always true: a *reduction reaction is also an oxidation reaction*. If in a chemical reaction, one element loses in positive valence (reduction) another element must gain in positive valence (oxidation). The substance which is reduced is the *oxidizing agent* and the substance which is oxidized is the *reducing agent*.

Preparation

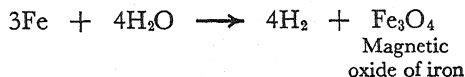
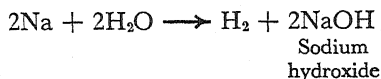
There are a number of methods of preparing hydrogen commercially or in the laboratory.

1. *From water.* (a) Electrolysis. This is the electrolysis of water which has been studied earlier. Hydrogen is prepared commercially by either this method or the water gas method.



(b) Metals and water. Some metals are very readily oxidized from the free state to a compound. These metals will react with water to form hydrogen and either an oxide or an hydroxide.

Metal + Water \longrightarrow Hydrogen + Oxide or Hydroxide

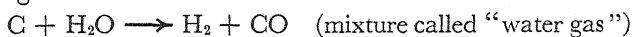


An activity series of the metals has been prepared which shows their relative reactivity. This is called the Electromotive Series Chart and is arranged with the most active elements at the top of the series. These are the elements which will react with water. Elements lower on the chart such as iron react more rapidly with steam. Elements below these react very slightly even with steam, while elements below hydrogen do not react at all.

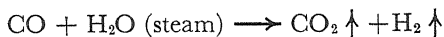
Since our cooking utensils are for the most part made of metals, this reaction is well to bear in mind. Many of the pots and pans on the market are alloys. These are mixtures of metals and their reactivity is very markedly influenced by the alloying. Dow metal, for example, is not nearly as readily oxidized as pure magnesium. Iron utensils will react slowly with hot water to form small amounts of hydrogen. Pure aluminum will react readily with hot water, but the alloys from which most "aluminum" utensils are made react slowly. Nevertheless, a grayish white deposit of aluminum oxide may be detected on the inside of these pans after water is boiled in them. The oxide usually adheres tightly and protects the pans from further action until it is dissolved off by an acid food.



(c) Nonmetal + water. Water gas is a mixture of carbon monoxide and hydrogen, produced by the reaction of steam on hot coke. It is frequently used as a fuel in the mixture, and is the "gas" which is sold by gas works to homes in areas which do not have natural gas. It is produced in furnaces which have alternate drafts of air and then of steam forced through them. The forced air heats coke to a bright red glow. The steam reacts with this very hot coke to produce carbon monoxide and hydrogen, but cools the coke. Then a new blast of air heats the coke again. The gases given off during the steam period are collected in the gas tanks.



The hydrogen is also produced pure by a modification of this process in which the carbon monoxide is removed. It may either be removed by cooling and condensing the carbon monoxide as a liquid, or it may be oxidized to carbon dioxide and the separation accomplished by absorbing the carbon dioxide in a solution with which it reacts.



Oxides of iron, chromium, or thorium act as catalysts for this reaction.

2. *From acids.* Any metal which occurs above hydrogen on the Electromotive Series Chart will react with acids to produce hydrogen and a salt.

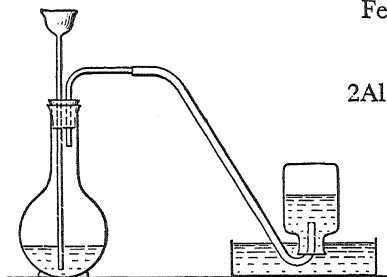
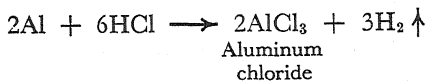
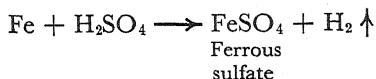


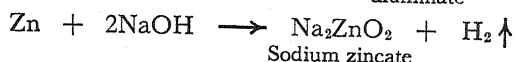
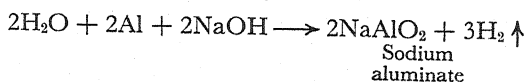
Fig. 6-2. Laboratory preparation of hydrogen from zinc and hydrochloric acid.

Electromotive Series Chart

- | | | |
|--------------|--------------|-------------|
| 1. Potassium | 6. Zinc | 11. Copper |
| 2. Sodium | 7. Iron | 12. Mercury |
| 3. Calcium | 8. Tin | 13. Silver |
| 4. Magnesium | 9. Lead | 14. Gold |
| 5. Aluminum | 10. Hydrogen | |

This is the general method most commonly used in the chemistry laboratory for the preparation of small amounts of hydrogen.

3. *From bases.* Aluminum and zinc will react with hydroxides to form hydrogen and sodium salts. These metals are present in the negative radical as if they were nonmetals.



Uses

Hydrogen has many uses commercially. Its use in gas for a domestic fuel has already been mentioned. It may also be used pure to produce very hot flames in oxy-hydrogen torches. These flames are hot enough to cut through metal by melting or burning the metal.

Hydrogen is also used to produce hydrogenated vegetable fats. The American housewife prefers to cook with solid fats, and most recipes are proportioned for the use of solid fats. There is no particular advantage to either solid or liquid fats. Many excellent cooks of Italian extraction will not use any fat except

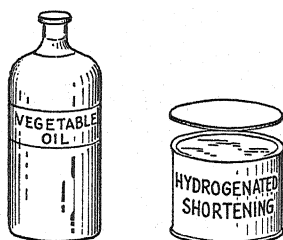


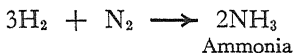
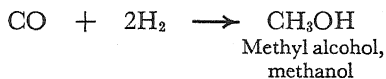
Fig. 6-3. Liquid vegetable oils react with hydrogen to produce a solid shortening.

olive oil if it is available. But traditions are such that it is profitable for the vegetable oils available on the American market to be changed into solid fats. The chemical difference between an oil and a solid fat is the amount of hydrogen held in the molecules which make up the mixture. Oils have less hydrogen than do solid fats. The molecules in the mixture of, say, corn oil have a smaller amount of hydrogen than do the molecules in the mixture of the very hard fat, mutton tallow. The physical properties of a fat may, therefore, be modified by changing the chemical composition of the molecules which make up the mix-

ture. When hydrogen is bubbled through an oil in the presence of a catalyst such as finely divided nickel, it reacts with the poorly hydrogenated molecules. The amount of hydrogen added to an oil regulates the resulting melting point, the more hydrogen added the higher the melting point and the harder the fat at room temperature.

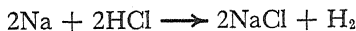
Hydrogen is also used in the gas sack of lighter-than-air craft. It is not as satisfactory as helium because of its inflammability, but its lifting power is greater than that of any other gas since its density is lowest. Helium, however, is available in the United States, but in few other countries except at high price. Helium does not have as great lifting power as hydrogen, but it does not burn.

Hydrogen is also used in many synthetic reactions. Examples are the catalytic production of methyl alcohol and of ammonia.



Equivalent Weights

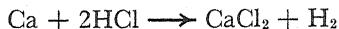
Since hydrogen combines with many elements and is replaced by others, and since the valences of all elements are not the same, a useful concept called the *equivalent weight* developed during the nineteenth century. *The gram equivalent weight of an element is the weight of the element which will combine with or replace 1.008 grams of hydrogen.* This weight of hydrogen contains 6.02×10^{23} atoms of hydrogen. The number of atoms of an element with a valence of plus one like sodium, which is *chemically equivalent* to this amount of hydrogen is 6.02×10^{23} atoms, or one gram atomic weight. In other words, one atom of sodium will take the place



of one atom of hydrogen, or 6.02×10^{23} atoms of sodium will take the place of 6.02×10^{23} atoms of hydrogen. The *gram equivalent weight* (equivalent weight expressed in grams) of sodium is equal to the *gram atomic weight*.

On the other hand, one atom of an element which has a valence of plus two, such as calcium, will replace two hydrogens.

This means that it will take only 3.01×10^{23} atoms of calcium to replace 6.02×10^{23} atoms of hydrogen. The gram equivalent weight of calcium is equal to *one-half* the gram atomic weight.



If other elements with positive and negative valences are considered, it is soon recognized that the gram equivalent weight is equal to the gram atomic weight of an element divided by the valence.

$$\frac{\text{Gram atomic weight}}{\text{Valence}} = \text{Gram equivalent weight}$$

Since 1.008 grams of hydrogen is equivalent to 8.000 grams of oxygen, the equivalent weight may be defined in terms of oxygen. Often in the laboratory it is more convenient to measure the amount of oxygen with which a given quantity of an element combines, than to measure the amount of hydrogen with which it combines or which it replaces. In terms of oxygen, *the gram equivalent weight of an element is the weight which combines with or replaces 8.000 grams of oxygen.*

NEW TERMS

Electromotive Series, hydrogenation, reduction, reducing agent, equivalent weight.

QUESTIONS

1. The hydrogen molecule has two atoms to the molecule. Give one line of evidence to support this.
2. Give balanced equations for the combination of hydrogen with oxygen, sulfur, chlorine, and nitrogen.
3. Why do we say that hydrogen does not support combustion?
4. When water is boiled in a shiny aluminum pan, a gray deposit is left on the pan. What is it? Is it a good idea to scour the pan thoroughly and remove this deposit? Why does the deposit disappear when an acid food such as tomatoes is cooked in the pan?
5. Name three metals which will displace hydrogen from water. Give balanced equations for each reaction. Name three metals which will displace hydrogen from hydrochloric acid. Give balanced equations.
6. Give several uses for hydrogen and explain each one.
7. What does the Electromotive Series of Elements tell us? For what type of reactions is it useful?

Gases, Liquids, and Solids

THE KINETIC THEORY

It has been pointed out in the first chapter that man has been interested in the nature of matter since he first began to think. At least early records indicate that some men were pondering the problem even then. You too have undoubtedly asked many questions about it, although you may not have asked formally about "the nature of matter." The problem is not completely solved by any means yet, although scientists have made extensive observations and have deduced some very workable theories.

You will remember how the scientific method works and how theories are developed. First numerous observations are made. Then in attempting to explain and correlate these observations a theory is evolved. As observations multiply, the theory is modified or abandoned in favor of a new theory which more adequately explains the observations. This procedure has occurred in the development of the Kinetic Theory. The observations and the laws which are generalizations of these observations will first be studied and then the theory and how it explains the laws.

Everything in the world is either a gas, a liquid, or a solid. An attempt to differentiate these states of matter brings recognition that volume and shape are the most useful criteria.

Gas	No definite volume	No definite shape
Liquid	Definite volume	No definite shape
Solid	Definite volume	Definite shape

The state of matter depends, of course, on the temperature and pressure at which the object is existing. A chemical substance

usually may exist in all three states, although some compounds which are rather easily decomposed, do not exist as gases. Water is a familiar example of a substance which occurs in these three states. You know water as steam (gas), liquid water, and ice (solid) and you recognize that the state depends on the temperature and pressure to which it is subjected. The Kinetic Theory explains the states of matter and changes in state.

GASES

When simple experiments are set up to study the properties of gases, it is soon found that in this state matter has the properties of (1) pressure, (2) compressibility, (3) infinite expansion, and (4) diffusion. These properties have been observed in daily life: the pressure of air in a tire and the possibility of adding more air and compressing it into the same space, the expansion of gas bubbles in a baking cake or in a sealed bottle when it is heated, the spreading of a gas with an odor. These observations from daily life illustrate the properties of gases. And there are numerous simple experiments which may be set up in the laboratory to demonstrate these properties.

A *vapor* is the gaseous phase of a substance which commonly exists at room temperature as a liquid or solid.

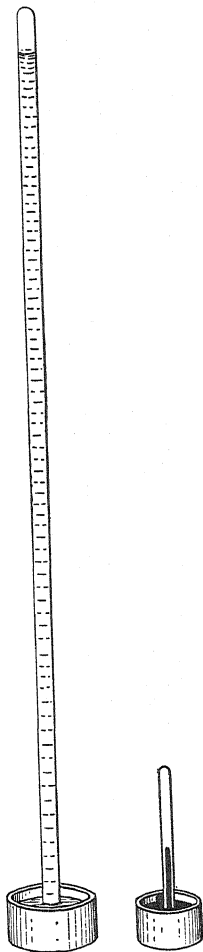
1. *Pressure.* The atmosphere is a mixture of gases and, like any gaseous mixture, exerts a pressure. An "empty" bottle may have a sheet of rubber stretched over the top and that sheet will not bulge either up or down. The air on top of the rubber sheet exerts as much pressure as the air in the bottle. Now, suppose that the bottle is provided with a tube through which the air may be withdrawn. As the air is pumped out of the bottle, the rubber sheet stretches farther and farther into the bottle. The air on the outside is forcing the rubber sheet into the bottle. It is interesting that this will occur, no matter what the position of the bottle. If the bottle is held upside down, the sheet is forced by the air *up* into the bottle. In other words, air exerts a pressure and it exerts it in all directions. If in another experiment air is forced into the bottle, the rubber sheet will bulge out.

The *barometer* is a device for measuring the pressure of gases. A simple form of a barometer may be made by filling with

mercury a long tube closed at one end and inverting it in a dish of mercury. The mercury will fall for a short way in the tube and then will remain steady at a definite height. If measurements are taken of the height of the column of mercury for several days, it is found that there is a slight variation in the position of the top of the mercury. There is no gas at all, but a vacuum in the closed tube above the mercury (actually there will be a very minute amount of mercury vapor), while the surface of the mercury in the dish will be subjected to the pressure of the air. Now when a pressure is exerted on a liquid, it is transmitted through that liquid undiminished. The pressure of the air on the surface of mercury is sufficient to hold up the column of mercury. Variations in the height of the mercury reflect the small variations in the pressure of the atmosphere from day to day.

The pressure is measured in terms of the height of the mercury column. This may be used as a measure because the bore of the tube does not influence the height of the column. A tube 5 centimeters in diameter will have a column of mercury as high as a tube 5 millimeters in diameter. At sea level the barometer stands at approximately 760 millimeters or 29.92 inches and the atmospheric pressure is said to be "760 millimeters" or in the English system "29.92 inches." The pressure at sea level will vary from day to day, as it does any place. At higher altitudes the pressure is lower.

Fig. 7-1. Barometers for measuring air pressure. The one on the left contains water and stands 13.6 times as high as the mercury barometer on the right. Why? Mercury is a better fluid for a barometer than water since it has a very low vapor pressure at room temperature.



It is possible to construct a barometer of any liquid. The chief advantage of mercury is that it has a very slight tendency to change to a gas at ordinary temperatures and the space above the mercury in the closed tube is therefore almost free of gas molecules. If water is used as the liquid in the tube, the space above the water soon has a rather high concentration of water molecules. They exert a pressure and push down on the column, introducing an error. A second advantage of mercury is its relatively high density, 13.55 grams per milliliter at $20^{\circ}\text{C}.$, which gives a fairly short column. A column of 760 millimeters of mercury corresponds to a column of 10,298 millimeters of water. This represents a pressure of about 15 pounds per square inch.

In measuring the pressure of gases at high pressure the unit usually used is the "atmosphere." *An atmosphere of pressure is equal to 760 millimeters of pressure.* A pressure of 200 atmospheres is, therefore, a pressure of 200 times 760 millimeters.

2 and 3. *Compression and expansion.* These properties may be demonstrated in any simple apparatus which allows for variation

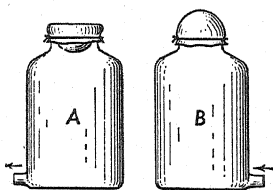


Fig. 7-2. *Demonstration of the pressure of air. A sheet of rubber is stretched over the neck of a bottle and fastened by an airtight binding. When air is pumped out of the bottle, the pressure of the air outside the bottle forces the rubber down into the bottle. When air is forced into bottle B, the greater pressure forces the rubber up.*

in pressure of the gas. If a bottle is fitted with a movable piston, without losing any of the gas in the bottle, it can be pushed down and will compress the gas. The gas is, of course, not infinitely compressible. Or the piston can be pulled out, not allowing any gas to enter the bottle, and expand the gas.

4. *Diffusion.* The diffusion of a substance is the ability of the substance to spread out uniformly through a given volume. For example bromine gas is added to a bottle until the color of the air-bromine mixture is a dark brown. If another bottle of air is placed mouth down over the mouth of the bottle filled with bromine, the brown color will move up into the top bottle and slowly the color of the gas mixture in the two bottles will become uniform. The bromine has diffused into the air to produce a uniform mixture.

In large volumes the tendency of gases to diffuse is influenced by the force of gravity on the denser gases. Hydrogen released into the atmosphere will diffuse through it, but will ultimately

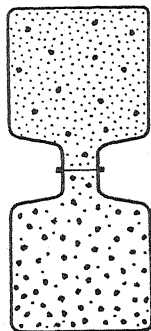


Fig. 7-3. Diffusion of gases. When two gases are brought together, each will penetrate into the other until a uniform mixture is formed. This is the process of diffusion.

accumulate in the upper atmosphere. A dense gas will diffuse, but it will accumulate near the ground or in cellars.

Gas Laws

Boyle's Law Boyle discovered that there is a direct relationship between the pressure and the volume of a gas. *Boyle's law: The volume of a given weight of gas varies inversely with the pressure if the temperature remains constant.* In other words, as the pressure increases, the volume decreases. Or as the pressure is decreased on a gas, the volume increases. This is a quantitative relation-

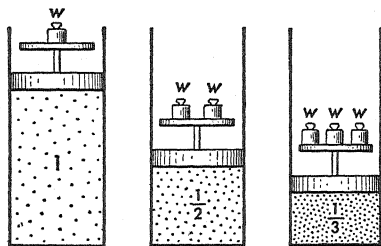


Fig. 7-4. Pressure and volume. A cylinder is provided with a piston to demonstrate the relation of pressure and volume in gases. When one weight, W , is placed on the platform of the piston, the volume of the gas is 1. When two weights, W , or twice

the pressure, are placed on the platform, the volume is $\frac{1}{2}$. When three weights or three times the pressure are placed on the platform, the volume is $\frac{1}{3}$. The number of gas molecules inside the cylinder is the same in each case.

ship, and what volume a given quantity of gas will occupy under changed pressure can be calculated. For a given quantity of gas,

the volume (V) multiplied by the pressure (P) is equal to a constant; it always equals the same number, a constant (k).

$$PV = k$$

It does not matter what the volume or pressure is for *this given quantity of gas*, the constant will always be the same. Therefore, for a new pressure, P_1 , and new volume, V_1 , with the same quantity of gas, the same constant is produced:

$$P_1V_1 = k$$

or

$$P_1V_1 = k = PV$$

Since the product of the original pressure, P , and the original volume, V , equals the same number, k , then:

$$P_1V_1 = PV$$

For a different quantity of gas, the "constant" will be another number.

The relation of pressure and volume in gases is so much a part of everyday experience that you need not memorize the mathematical formula of Boyle's law, but you can carry out the calculation by a "common sense" method that you will never forget. The new volume is equal to the old volume multiplied by a fraction made up of the old and new pressures. If the pressure change is such that an increase in volume will occur, the old volume must be multiplied by a number *greater* than one. To do this the larger pressure is placed in the numerator and the smaller pressure in the denominator. If, when you read through the problem, you anticipate that the volume will decrease, the old volume is multiplied by a fraction *less* than one. The smaller pressure becomes the numerator and the larger the denominator. If you think through every problem and anticipate whether a gas expands or contracts (the volume grows larger or smaller) you will be able to do these calculations years from now.

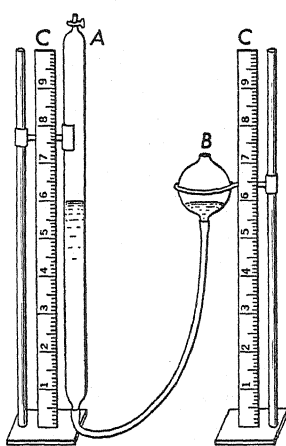
EXAMPLE: Calculate the volume which 100 milliliters of gas will occupy if the pressure is increased from 700 millimeters to 750 millimeters.

$$V = 100 \text{ ml.} \times \frac{700}{750} = 93.4 \text{ ml. at 750 mm.}$$

The calculation may be carried out either by memorizing the formula, $PV = P_1V_1$, or by the "common sense" method. In

the latter method it is seen that the new volume is equal to the old volume multiplied by some fraction. That fraction will be composed of the numbers which are the old and the new pressures. The number which will be in the numerator is determined by anticipating as you read the problem whether the volume will increase or decrease. If the volume will increase, the large number is placed on top; if it will decrease, the small number is placed on top. Thus, when you read the above problem, you realize that since the pressure is increasing, the volume will decrease. Therefore we write a fraction with the small number in the numerator; $700/50$ is used. The advantage of this method

Fig. 7-5. Apparatus for verifying Boyle's Law. Eudiometer A contains a fixed amount of gas when the stopcock is closed. The level of mercury in the eudiometer and in the leveling bulb B are the same when the pressure in the eudiometer is equal to atmospheric. If the level of mercury in the eudiometer is above that in the bulb, the pressure of the gas is equal to atmospheric minus the difference in levels. The meter sticks, C, are used to measure the heights of the mercury in bulb and eudiometer.



lies in the fact that one quickly forgets formulas, but one has had enough experience with gases to know almost intuitively that when they are squeezed they compress.

It is possible to verify Boyle's law by a fairly simple experiment. A eudiometer (graduated tube closed at one end) with a stopcock is connected by means of rubber tubing with a leveling bulb. The bulb is filled with mercury and it rises in the eudiometer until the level in the bulb and in the eudiometer are equal. The stopcock is closed and the volume of air read. The pressure on the mercury in the bulb (atmospheric) is equal to the pressure on the mercury in the eudiometer. The leveling bulb is raised, causing the mercury in the bulb to stand above the mercury in the eudiometer. The pressure of the air in the eudiometer is now greater than atmospheric by the difference in

these levels and the volume of air is smaller. For example, if atmospheric pressure is 760 millimeters and the mercury in the bulb stands 100 millimeters above the mercury in the eudiometer, the air in the eudiometer must be pressing the mercury down with a force of $760 + 100$ or 860 millimeters. Numerous readings of the volume of the air which has been trapped, at pressures both above and below atmospheric might give data like this:

<i>Volume</i>	<i>Pressure</i>	<i>Product, $P \times V$</i>
100 ml.	760 mm.	76,000
95	800	76,000
84.4	900	76,000
108.6	700	76,000
126.7	600	76,000

Your data will probably not give as precise results because of the errors which you introduce into the experiment.

Careful measurement, which avoids as many errors as possible, shows that at ordinary temperatures and pressures, the product of the temperature and the pressure is remarkably constant. At very high pressures, deviations from the law become great.

Charles' Law You are familiar with the fact that a gas tends to expand as its temperature rises. If the pressure of the gas is kept constant, the increase in volume is $\frac{1}{273}$ of the original volume of the gas at 0°C. , for each one degree centigrade rise in temperature. Likewise for ordinary temperatures, the decrease in volume is $\frac{1}{273}$ of the original volume of 0°C. , for each one degree centigrade drop in temperature. If this were true for all temperatures, the volume of the gas at -273°C. would be zero. This

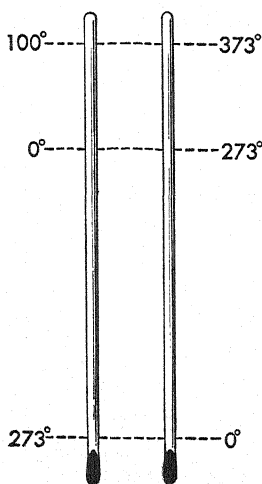


Fig. 7-6. Comparison of the centigrade and absolute (or Kelvin) temperature scales.

never occurs. All gases change to liquids before -273°C. is reached. However, because of this relation, -273°C. is called *absolute zero*.

The Absolute Scale (or Kelvin Scale) has been constructed around the absolute zero. It is a scale whose intervals correspond to the intervals on the centigrade scale, but with zero 273 degrees below the zero on the centigrade scale. Thus a reading on centigrade may be converted to a reading on absolute by adding 273 degrees.

<i>Centigrade</i>	<i>Absolute</i>
-273°	0°
0°	273°
100°	373°

Using the absolute scale, a simple expression of the relation of the volume and the temperature of a gas at constant pressure is obtained. Charles' law states: *The volume of a gas varies directly as the absolute temperature, if the pressure on the gas is constant.* In other words, as the temperature rises the volume increases.

$$V = kT, \quad V_1 = kT_1.$$

For the same amount of gas,

$$\frac{V}{T} = k = \frac{V_1}{T_1}.$$

Therefore the change in the volume of a gas which will occur when the temperature of a gas changes can be calculated.

EXAMPLE: Calculate the volume occupied by 100 milliliters of a gas at 20°C. , when its temperature is increased to 40°C.

$$\begin{aligned} 20^{\circ}\text{C.} &= 293^{\circ}\text{A.} & 40^{\circ}\text{C.} &= 313^{\circ}\text{A.} \\ V &= 100\text{ ml.} \times \frac{313}{293} = 106.8\text{ ml.} \end{aligned}$$

These problems may also be calculated by either learning the formula or by the "common sense" method. In this method again we anticipate whether the volume will increase or decrease and then set up a fraction with the large number in the numerator if the volume will increase and with the small number in the numerator if it will decrease. In this problem the temperature will increase and therefore the volume will increase. The

higher temperature, 313, is then placed over the lower temperature, 293. You must always use absolute temperature. The volume does *not* vary directly with the centigrade temperature.

The *Standard Temperature* is 0° C. or 273° absolute. The *Standard Pressure* is 760 millimeters. Since the volumes of gases vary so markedly with temperature and pressure, they are usually described under these Standard conditions.

Dalton's Law of Partial Pressures Dalton concluded, after a large number of experiments on mixtures of gases, that *the pressure exerted by a mixture of gases is equal to the sum of the pressures of the individual gases*. Thus the pressure of the air is equal to the sum of the pressure of the nitrogen plus the pressure of the oxygen, plus the pressure of each of the other gases present in it.

$$P = P_1 + P_2 + P_3 + P_4 + \dots$$

This law is used in dealing with any mixture of gases. You will have occasion to use it in the laboratory when gases are collected over water and therefore contain water vapor. If the level of the water in the bottle is the same as the level outside the bottle in the pneumatic trough, the pressures of the gases in the bottle are the same as atmospheric. If on the day oxygen is prepared the atmospheric pressure is 750 millimeters, then the pressure of the oxygen PLUS WATER VAPOR is equal to 750 millimeters.

$$P_{O_2} + P_{H_2O} = 750 \text{ mm.}$$

When gas is collected over water and each small bubble passes through the water, the gas becomes *saturated* with water vapor. The quantity of water vapor for saturation increases with a rise in temperature, and it has been determined for every temperature. Suppose that the temperature of the gas and water was found to be 20° C. Reference to the table in the Appendix shows that the pressure of water vapor at saturation at 20° is 17.5 millimeters. (Notice that it varies with temperature.) The pressure of the oxygen can be calculated.

$$P_{H_2O} = 17.5$$

$$P_{O_2} = 750 - 17.5 \text{ mm.} = 732.5 \text{ mm.}$$

The water vapor pressure is sometimes called the *aqueous tension*.

All three of these laws may be combined in a calculation where the pressure and the temperature of a gas are changing.

EXAMPLE: Calculate the volume of a gas at standard conditions if it occupies a volume of 250 milliliters at 20° C. and 750 millimeters. The new volume will be equal to the old volume times the pressure fraction. Here the pressure will change from 750 millimeters to 760 (Standard Pressure), an increase, and the volume will therefore decrease and our fraction must be less than one. $V = 250 \text{ ml.} \times \frac{750}{760}$. This will be multiplied by the absolute temperature fraction. Since the temperature will change from 293° absolute (20° C.) to 273 absolute (0° C. and Standard Temperature), a decrease; the volume will, therefore, decrease and the temperature fraction should be less than one. This will then give:

$$V = 250 \text{ ml.} \times \frac{750}{760} \times \frac{273}{293} = 229.9 \text{ ml.}$$

Dalton's law may also be used along with the other laws in one calculation.

EXAMPLE: A volume of 120 milliliters of oxygen is collected over water in the laboratory at 25° C. and 720 millimeters pressure. What volume will the dry oxygen occupy at standard conditions?

The problem is solved in the same manner as the above one, except that the pressure of oxygen must be calculated. The pressure given in the problem, 720 millimeters, is the pressure of a mixture of gases, oxygen, and water vapor. By referring to the water vapor pressure table in the Appendix, it is found that the pressure of water vapor at saturation at 25° C. is 23.8 mm. Therefore:

$$P_{O_2} = 720 - 23.8$$

The problem will be set up:

$$V = 120 \times \frac{720 - 23.8}{760} \times \frac{273^\circ}{298^\circ} = 102.4 \text{ ml.}$$

Pressure and Temperature *If the volume of a gas remains constant, an increase in temperature results in an increase of pressure.* This observation was formulated into a law by Gay-Lussac, and you have probably anticipated this mathematical relationship from the laws of Boyle and Charles.

EXAMPLE: A bottle of gas containing 200 milliliters is sealed and then warmed from 0° C. to 100° C. If the original pressure was 760 millimeters, what is the final pressure?

The new pressure will be equal to the old pressure multiplied by the absolute temperature fraction. The temperature is increased, therefore the pressure will be increased and the fraction must be greater than one.

$$P = 760 \text{ mm.} \times \frac{373}{273} = 1038 \text{ mm.}$$

The Gram Molecular Volume

If 1 gram molecular weight of a gas is weighed out and the volume is determined at standard temperature and pressure, it is always 22.4 liters. This volume is called the *gram molecular volume* and is a very convenient number to remember. Thus 2.016 grams of hydrogen, H_2 , will occupy 22.4 liters at standard conditions.

32.00 grams of oxygen, O_2 , will occupy 22.4 l. at S.C.

44.005 grams of carbon dioxide, CO_2 , will occupy 22.4 l. at S.C.

28.016 grams of nitrogen, N_2 , will occupy 22.4 l. at S.C.

4.003 grams of helium, He , will occupy 22.4 l. at S.C.

When you remember this fact, you can always calculate the weight of any given volume of gas. If you know that 22.4 liters of the gas at standard conditions contains 1 gram molecular weight, you can calculate the weight of any other volume at standard conditions, since it will be a direct proportion. Likewise, if you wish to calculate the weight of a volume of gas which is not measured at standard conditions, you can calculate from the gas laws what the volume of that quantity of gas would be at standard conditions and then what the weight will be.

PROBLEM: Calculate the weight of 1 liter of hydrogen gas at standard conditions.

ANSWER: The gram molecular weight of hydrogen, H_2 , will be twice the atomic weight.

$$2 \times 1.008 \text{ g.} = 2.016 \text{ g.}$$

2.016 grams of H_2 will occupy 22.4 liters at standard conditions. Therefore,

$$\frac{x \text{ g.}}{2.016 \text{ g.}} = \frac{1 \text{ l.}}{22.4 \text{ l.}}$$

$$x = 0.081 \text{ g., weight of 1 l.}$$

PROBLEM: Calculate the weight of 1 liter of ethylene, C_2H_4 , at 740 mm. pressure and $25^\circ C$.

ANSWER: First calculate the volume which 1 liter of ethylene at 740 mm. pressure and $25^\circ C$. would occupy at standard conditions,

$$V = 1 \text{ l.} \times \frac{740 \text{ mm.}}{760 \text{ mm.}} \times \frac{273^\circ}{298^\circ} = 0.89 \text{ l. at S.C.}$$

Then calculate the weight of this volume of gas. The gram molecular weight of ethylene, C_2H_4 , is 28.042 ($24.01 + 4.032$). Therefore,

$$\frac{0.89 \text{ l.}}{22.4 \text{ l.}} = \frac{x \text{ g.}}{28.042 \text{ g.}}$$

$x = 1.11 \text{ g., weight of } 0.89 \text{ l. of ethylene at S.C. or of 1 liter at } 740 \text{ mm. and } 25^\circ C.$

Kinetic Theory Applied to Gases

A theory which explains the behavior of gases will have to answer a number of questions.

Why are gases infinitely expansible?

Why do gases exert pressure equally in all directions?

Why are gases so light, so low in density?

Why do gases intermingle and form a homogeneous mixture?

Why is the total pressure of a mixture of gases equal to the sum of the individual pressures?

Why does the pressure increase with the temperature when the volume is constant?

Why does the volume increase with the temperature when the pressure is constant?

The Kinetic Theory can explain all these questions.

You will remember that the Particle Theory of Matter was discussed in Chapter 2 when the nature of matter was first described and some simple demonstrations were given which, along with other types of experiments, have led men to think that all matter is composed of very small particles, the molecules. This is true of matter in all its states. This is a fundamental assumption of the Kinetic Theory.

Assumptions of the Kinetic Theory

The Kinetic Theory states that:

1. The molecules of a gas are relatively far apart and have little attraction for one another.
2. The molecules of a gas move very rapidly.
3. The molecules of a gas move more rapidly as the temperature increases.
4. The molecules of a gas are perfectly elastic. Any collisions of molecules with each other or with the sides of the container cause no loss of energy.
5. The average kinetic energy of molecules of a gas at the same temperature, is equal and is the product of the mass (m) of the molecules times the velocity (v) squared. K.E. (kinetic energy) = kmv^2 .

On the basis of this theory it is understandable why gases are infinitely expandable. If the molecules are moving rapidly, they can spread out until they fill all the space available. The distance between the molecules will increase when this occurs. The pressure which gases exert is the result of the tiny individual molecules hitting the sides of the container. They will move in all directions and there will be as great a probability of a given number hitting the bottom of the container at a given instant, as there will be of the same number hitting the top of the container. The great spaces between the molecules will allow different molecules to intermingle completely and uniformly with the original gas. The great spaces in between the molecules also account for the very low density of gases. Gases diffuse, even against gravity, because of the rapid movement of the particles in all directions, and because the size of the individual molecules is so small that the force of gravity on each particle is relatively slight.

Application of Kinetic Theory to Gas Laws

Boyle's law is explained by the Kinetic Theory which shows why an increase of pressure on the gas should decrease the volume of the gas. The great spaces between the molecules are reduced when the pressure increases. The pressure on a gas is equal to the pressure of the gas. If the volume is reduced by one-half, and the temperature of the gas is constant so that the velocity of the molecules is constant, then the molecules will hit

the sides of the container twice as often and the pressure will hence be twice as great.

Charles' law may be accounted for very adequately by the Kinetic Theory. If the absolute temperature of a gas is doubled, it is observed that the volume will double providing the pressure is constant. Now according to the Kinetic Theory, increasing the absolute temperature will increase the kinetic energy. Since the kinetic energy is a function of the mass and the velocity, and since the mass of the molecules will not change, the velocity must increase. This means that the molecules hit the sides of the container more frequently, and if the pressure on the outside is maintained constant, the bombarding molecules will push the sides of the container out and produce an increase in volume.

Dalton's law may likewise be explained by the Kinetic Theory. The pressure of a gas, it has been pointed out, is the result of the bombardment of the molecules on the walls of the container. The magnitude of the pressure depends on the frequency with which molecules hit the sides and the momentum (mass \times velocity²) of those individual molecules. The total pressure of a mixture of gases will then be the sum of the pressures of all the molecules hitting the sides. It will be similar to the situation which would arise if two students together pushed on a door. The force on the door would be the force with which one student pushed, plus the force with which the other pushed and whether both had curly hair or white skin would not add or detract from the pressure.

The behavior of gases can be explained therefore on the basis of the Kinetic Theory. It will be seen that the theory is extended to liquids and solids, and explains their behavior as well as the conversion of one state to another.

LIQUIDS

Liquids and their properties are so much a part of daily experience that they seem almost "common sense." When water is poured into a pitcher, it is expected that it will assume the shape of the pitcher and you would be very surprised, indeed, if it did not. You also expect the volume to be relatively constant. If you pour out a cup of cold milk, you expect that when it has warmed slightly it will still be approximately one cup.

You do know that the volume is not absolutely constant with temperature, since you have probably had the experience of water spilling out of a full kettle when it is heated. You know

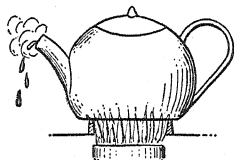


Fig. 7-7. A full kettle overflows when it is heated and the water expands.

from experience that some liquids pour more readily than others. You know that oil floats on water, but that alcohol mixes with it.

These are some of the observations encompassing the most striking properties of liquids. When experiences are generalized and when in the laboratory these observations are simplified so that the complexity of the situation is not misleading, the properties of liquids can be stated in simple, although formal, terms.

Liquids may be differentiated from gases and solids on the basis of volume and shape. Liquids have definite volume but not definite shape.

Viscosity

Viscosity is the term used to describe quantitatively the difference in liquids to pouring. *Viscosity is a measure of the resistance of a liquid to flow.* The viscosity of a liquid may be described in terms of the length of time which it takes for a given quantity of liquid to flow through a given tube. It is possible to make such rough measures in the kitchen with an ordinary funnel. The

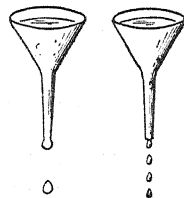


Fig. 7-8. Viscosity. These two funnels with narrow bore stems show the difference in viscosity (resistance to flow) between two liquids. The one on the left has a much higher viscosity than the one on the right.

length of time it takes one cup of water to flow through the stem of a funnel might be compared with the length of time it would take one cup of molasses to flow through the same funnel. In daily life units of viscosity are not used very frequently. You do

ask, however, for "30 weight oil" in summer for your automobiles, and "10 weight oil" in very cold weather. The "30 weight" oil has a higher viscosity than the "10 weight." In experimental foods work, viscosity is sometimes a valuable measurement. For example in studying jellies, the viscosity of the pectin solution is a measure of the jellying power of that solution; a pectin with a high viscosity is able to produce a firm jelly. The viscosity of liquids varies from liquids with low viscosity to those with high, but all liquids show an *increase* in viscosity as the temperature *decreases*. You say, "Slow as molasses in January." You see tar being heated to decrease its viscosity. The viscosity of a liquid, then, varies with the temperature.



Fig. 7-9. Baker-Ostwald pipet for determining the relative viscosity of pectin solutions. The solution is drawn up into the pipet until it is almost full. The pipet is inverted, and the length of time necessary for the solution to flow between the two marks is carefully measured. The temperature must be controlled since viscosity varies with temperature.

Surface Tension

Liquids act as if their surface was a tight, elastic skin, stretched over the liquid and protecting it from penetration. You see water

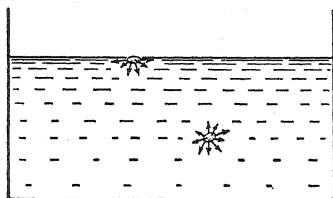


Fig. 7-10. Surface tension. Force is exerted on the molecule on the surface, downward and sideward, but on the molecule in the body of the liquid, force is exerted in all directions by the neighboring molecules. The unequal force on the surface molecules causes them to pack together and form a tight "skin."

bugs gliding on the surface of a pond; you can float a needle on a glass of water; you see globules of water running down a dirty windshield instead of spreading out on it; molten lead dropped through a tower forms perfect spheres. These phenomena are

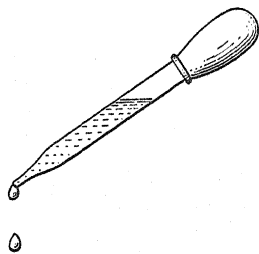
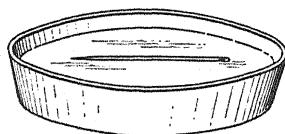


Fig. 7-11. Drops of water forming and falling.

Fig. 7-12. A needle floats on the surface of a dish of water. The surface tension supports it. If the surface is broken by the point of the needle, it will fall to the bottom of the dish.



the result of *surface tension*. It is defined as the *force acting in the surface of liquids which tends to reduce the superficial surface to a minimum*. The surface tension of a liquid may be measured quantitatively and varies from one liquid to another.

A wetting agent is a substance which decreases the surface tension of a liquid, usually water. If a drop of liquid soap is added to the water on which a needle is floating, the needle will immediately sink to the bottom. The soap has diminished the surface tension of

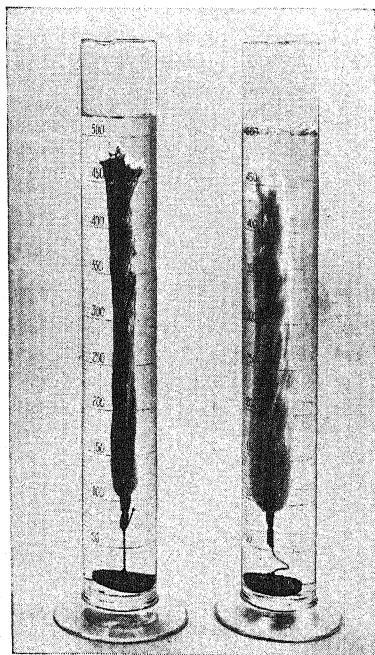


Fig. 7-13. Clarkson and Draves Wetting Test. This test is a measure of the wetting and penetrating action when a wetting agent is added to water. The fibers are a standard unbleached raw cotton yarn. The cylinder on the left contains pure water, while that on the right contains a wetting agent and water. (Courtesy of the Atlantic Refining Company.)

the water and it no longer supports the needle. There are a great many wetting agents produced with various properties. Wetting agents are commonly added to dye baths in order that the fabric may be wetted uniformly and hence dyed evenly. Wetting agents are added to garden sprays in order that the solution may spread over the leaves of the plant and protect all parts of them. They are added to inks in order that the colored particles may be evenly dispersed. Soaps act as wetting agents and allow the water to penetrate the fabric and come between the soil and the fiber. The soil may then be removed.

The Kinetic Theory Applied to Liquids

The Kinetic Theory explains the behavior of liquids very well. The assumptions of the Kinetic Theory are the following:

1. In liquids, the molecules are relatively close together.
2. In liquids, the molecules are moving.
3. The movement of the molecules increases with an increase in temperature.
4. The collisions of molecules are perfectly elastic and no energy is lost.
5. In liquids the molecules exert some attraction for one another. (This is called the Van der Waals forces and opposes the kinetic force which tends to make a liquid fly apart and become a gas.)

A liquid has constant volume because the Van der Waals forces tend to hold the molecules close together, but it can be poured because the molecules can move over one another. The viscosity of a liquid is more or less a measure of the Van der Waals forces. If the attraction of the top layer of molecules for the next layer is great, then these molecules in the top layer will not slip by those in the next layer very readily and the viscosity will be high. It is likewise apparent that the surface tension of a liquid must be the result of Van der Waals forces. If one considers molecule *A* on the surface of a liquid and molecule *B* in the interior of a liquid, it is possible to understand the occurrence of surface tension. Molecule *A* is experiencing attraction of molecules on the sides and below it, but not on top. It is therefore attracted into the interior of the liquid. Molecule *B* is experiencing attraction in all directions. This will result in a tendency to hold the molecule stationary. In liquids where the Van

der Waals forces are great, the surface tension will be high: those surface molecules will be held down tightly and will form a skin over the liquid. In some liquids, the kinetic movement of the molecules will be great and the Van der Waals forces small. These liquids will have a low surface tension. A wetting agent adds another type of molecule to the surface, interferes with the Van der Waals forces between molecules, and breaks up this skin of molecules, decreasing the surface tension.

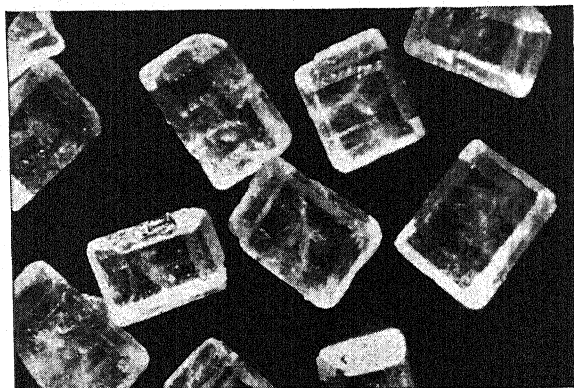


Fig. 7-14. Sugar crystals. Notice the regular shape of the crystals. (Courtesy of United States Beet Sugar Association.)

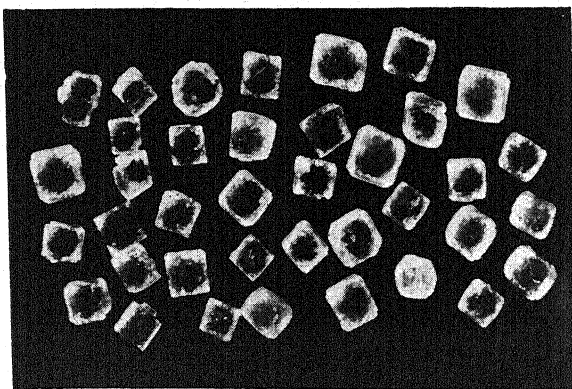


Fig. 7-15. Sodium chloride crystals produced by subsurface crystallization. (Courtesy of Diamond Crystal-Colonial Salt.)

SOLIDS

Solids are substances which have definite volume and definite shape. When pure solids, that is solids composed of one pure substance, are studied, it is often found that each has a charac-

teristic crystalline shape. Thus, sodium chloride crystals are tiny perfect cubes, whereas copper sulfate hydrate forms large blue triclinic crystals. (The terms used to describe various crystal shapes will not be studied. They may be found in a text on

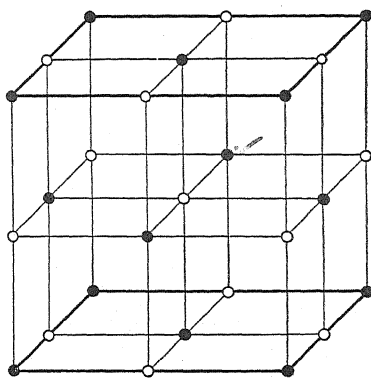


Fig. 7-16. Arrangement of centers of sodium and chloride ions in a sodium chloride crystal.

crystallography.) Of course, if these crystals are ground in a mortar, solid particles which do not have the characteristic shape will be produced. All pure solids do not have perfect crystalline shape.

The Kinetic Theory has the following assumptions concerning solids:

1. In solids, the movement of the molecules is relatively slow.
2. The Van der Waals forces in solids are relatively great.
3. The movement of the molecules increases with an increase in temperature.

In crystals of pure substances the perfect crystal structure is the result of the pattern in which the molecules or the ions are oriented. The rigidity of the crystal results from the scanty motion, vibration at most, of the molecules.

INTERCONVERSION OF STATES OF MATTER

Experience in everyday life teaches that not only do three states of matter, gas, liquid, and solid, exist, but these states may be changed into one another. Ice melts, a moth ball or gasoline has an odor, the windows "sweat." These are changes in the states of matter. (In order they are: solid to liquid, solid

to gas, liquid to gas, and gas to liquid.) You may not be observant enough to recognize that a change in a state of matter is always accompanied by a change in energy. However,

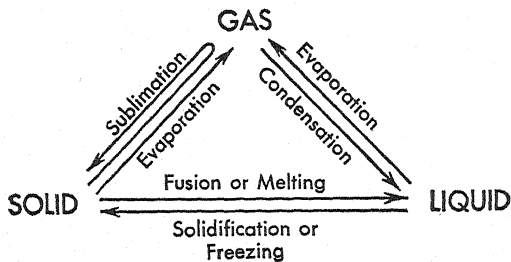


Fig. 7-17.

when this is pointed out, everyday experience will show that this is always true. Special names are given to these changes in the states of matter. They are summarized here in a diagram.

Liquefaction of Gases

Some gases are readily converted into liquids, if they are simply cooled. For example, if a mixture of air, composed of oxygen, nitrogen, carbon dioxide, and water vapor is cooled, the water will condense to a liquid, but the other substances will remain as gases. Water is the one gas in the mixture which exists most commonly at room temperature as a liquid. The others have very low boiling points (carbon dioxide sublimates) and exist commonly as gases at room temperature. In order to change them to liquids, it is necessary not only to cool them in order that the movement of the molecules will be slow, but also to compress them by the use of high pressure, in order that the molecules will be pushed together closely where their attraction for one another is great. This cooling of the gas is in reality the removal of energy from the gas. All gases can be liquefied if they are cooled and compressed sufficiently. It is found that all gases have *critical temperatures*, i.e., *temperatures above which they cannot be liquefied*. For example, the critical temperature of oxygen is $-118^{\circ}\text{C}.$, and it must be cooled at least to this temperature before it will change to a liquid. *The critical pressure is the pressure at the critical temperature necessary to liquefy the gas.* Below the critical temperature, the pressure necessary to liquefy the gas is not as great as at the critical temperature. Above the critical temperature, no amount of pressure will ever effect the conversion.

Critical Temperature of Some Common Gases

Gas	Formula	Critical Temperature	Critical Pressure
Hydrogen	H ₂	-239.9° C.	12.8 atm.
Nitrogen	N ₂	-147.1°	33.5
Oxygen	O ₂	-118.8°	49.7
Water	H ₂ O	374°	217.7
Ammonia	NH ₃	132.4°	111.5
Carbon dioxide	CO ₂	31.1°	73.0
Sulfur dioxide	SO ₂	157.2°	77.2
Freon	CCl ₂ F ₂	111.7°	39.4

The extent of the loss or gain in energy is characteristic of the substance at a given temperature. *The amount of heat which must be removed from a unit weight of gas in order to change it to the same weight of liquid is called the heat of condensation.* It is usually measured in terms of calories per gram. The same amount of heat must be taken from a gas in order to change it into a liquid as must be added to the liquid to turn it into a gas. In other words the heat of condensation is equal to the heat of vaporization, but opposite in sign. This is necessarily true, if the Law of Conservation of Energy is true. *The heat of vaporization is the amount of heat needed to change a unit weight of liquid into the same weight of gas, at a given temperature.* Thus at 100° C., it is necessary to remove 540 calories from 1 gram of water vapor in order to change it into 1 gram of liquid water. Or it is necessary to add 540 calories to 1 gram of liquid water in order to change it into 1 gram of water vapor. The first - 540 calories per gram is the heat of condensation, the other + 540 calories per gram is the heat of vaporization.

The Kinetic Theory explains this behavior. The gas molecules must be slowed down if they are to be in the liquid state. Since the kinetic energy of all molecules is directly proportional to the temperature, the gas must be cooled (energy must be removed) in order to slow down the molecules. The molecules must also move close together. Evidently some gases, such as water vapor molecules, do this if they are cooled. Other gaseous molecules, such as oxygen, must be pressed together under high pressures.

Vapor Pressure of Liquids

Liquids through the whole temperature range in which they exist show some tendency to change into a gas. Most liquids

will have a cloud of gas molecules above them. This tendency varies with different substances and increases with the temperature. Thus at 20°C . mercury has a very slight tendency to change to a gas, and the amount of vapor above the liquid is almost negligible, while alcohol has a decided tendency to vaporize and the amount of gas molecules above that liquid is large. Both of these liquids will show a greater tendency to vaporize at higher temperature. The pressure of the gaseous molecules above a liquid at a given temperature, is called the

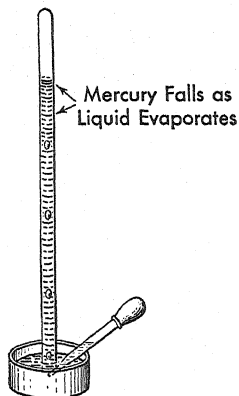


Fig. 7-18. Demonstration of the vapor pressure of a liquid. A liquid such as ether is admitted to the bottom of a column of mercury in a barometer. The droplets rise through the mercury since they have a lower density than it. As they evaporate into the space above the mercury, they exert pressure on it and push it down.

vapor pressure. The mercury molecules, which are few in number, will exert a small pressure while the alcohol molecules, which are more numerous, will exert a greater pressure.

This phenomenon is readily explained by the Kinetic Theory. At a given temperature, the *average* kinetic energy of the molecules of a liquid is always the same. But some molecules are moving more rapidly than the others, and some are moving more slowly. If a rapidly moving molecule reaches the surface, its kinetic energy may be great enough to overcome the attraction of the other molecules, and it may jump out of the liquid. In an enclosed space, for example a bottle with a stopper, the molecule will move around in the gaseous layer, striking the walls of the container and creating a pressure on them. The sum of the force of the molecules in the gaseous layer represents the vapor pressure of the liquid. In a closed bottle the same molecules are not always in the gaseous layer. As in most natural phenomena, there is *dynamic equilibrium*, a continual

change in the individual membership of each fraction, but no change in the balance. In the case of a closed bottle of liquid, suppose that at 20° C. there are 100 molecules in the gaseous layer when the system comes to equilibrium. Some of these 100 molecules will fall back into the liquid and lose their energy. Other molecules will pick up this energy, move more rapidly, and jump out of the liquid. Thus there will always be 100 molecules in the gaseous layer, but the personnel will continually change.

Evaporation

If the stopper is left out of a bottle and the liquid has a reasonably high vapor pressure, such as water, the volume of the liquid

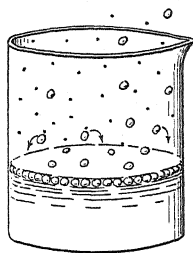


Fig. 7-19. Evaporation. Some of the fast-moving liquid molecules hop off the surface of the liquid and make their way between air molecules out of the beaker. Others collide with air molecules or the sides of the beaker and fall back into the liquid.

will gradually decrease. When the stopper is removed from the bottle, some molecules drift out of the bottle and lose the opportunity of ever falling back into the liquid. If a stream of air blows over the liquid, evaporation is much more rapid. You have seen clothes dry with amazing rapidity on a windy day. This, of course, is an accelerated version of the bottle with the stopper removed. Great numbers of gaseous molecules are removed and never have the opportunity to fall back into the liquid. If the rapidly moving molecules escape and never return, how do the remaining molecules gain enough energy ever to change to a gas? Your experience with evaporation from your own body gives the answer to this question. Pour a small amount of a very volatile liquid such as ether into the palm of your hand. It will evaporate rapidly and your hand will feel very cool. Stand in a breeze in a wet bathing suit, even on a hot day, and you will feel chilly. The slow moving molecules are left behind and the temperature of the liquid drops. Heat

is removed from the environment, in the cases above from your hand or body, and the slow molecules increase in speed. They too may then escape.

Boiling Point

If a liquid is heated, one may readily observe that the rate of evaporation increases. If the vapor pressure is measured, it shows an increase. Eventually the liquid begins to bubble — we

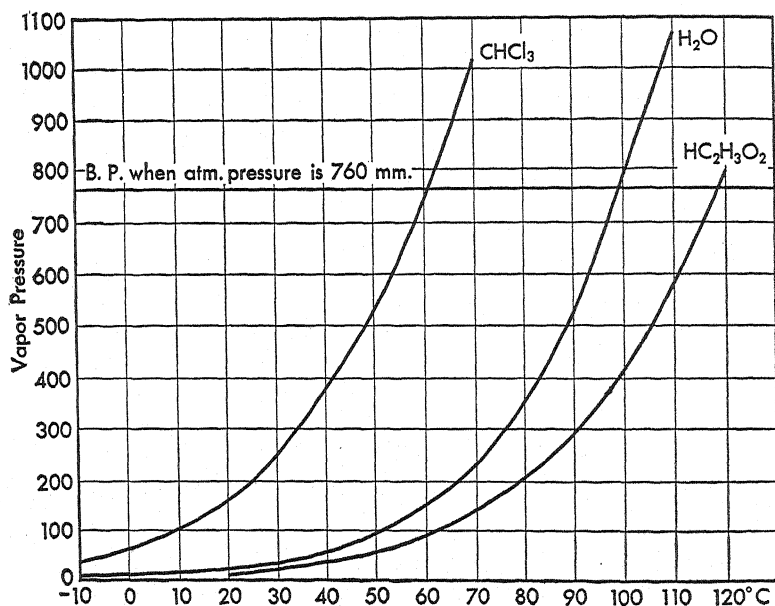


Fig. 7-20. Vapor pressure of chloroform, water, and acetic acid plotted against temperature.

say that it is "boiling." If a thermometer were in the liquid, it would be observed that the temperature climbs steadily, until the liquid reaches the "boil." It then remains steady. Careful study of the vapor pressure will reveal that this state which we call "boiling" occurs at a temperature where the vapor pressure just exceeds the pressure on the liquid. On days when the atmospheric pressure is low, the temperature at which the liquid boils will be a little lower than on days when the atmospheric pressure is higher. If the flask containing the liquid is connected with a

pump and the pressure on the liquid increased, the temperature will be much higher before the liquid boils. *The boiling point is the temperature at which the vapor pressure of the liquid just exceeds the pressure on the liquid.*

The Kinetic Theory explains boiling. When the pressure of the molecules escaping from the liquid just exceeds the pressure of air molecules on the liquid, the escaping molecules not only diffuse between the air molecules, but they are so numerous that they force the air molecules out of the flask and then pour out themselves. The bubbling which is noticed in boiling a liquid is the result of gaseous bubbles forming in the interior of the liquid. Below the boiling point, you can see them form at the bottom of a beaker where the temperature is higher than the temperature of the body of the liquid. They rise through the liquid and become smaller and smaller as they cool, until finally they disappear. At the boiling point, bubbles form at the bottom and rise, expanding in size as the pressure on them decreases and break on the surface of the liquid. The pressure on a bubble at the bottom of the beaker is equal to atmospheric pressure plus the height of the water above the bubble. At the surface it is equal to atmospheric pressure. This gaseous bubble will, of course, follow Boyle's law and expand as the pressure on it decreases.

Freezing

If a liquid is cooled, the temperature will drop steadily until the freezing point is reached; it will then remain steady until the liquid changes to a solid. Occasionally the temperature may drop a short interval below the freezing point, but as the solid crystals begin to form, it shoots back to the freezing point and remains steady until all the liquid becomes solid. The liquid is *supercooled* when its temperature is below the freezing point. This is a very unstable and transitory state. *The freezing point of a pure substance is that temperature at which solid and liquid may exist in equilibrium with one another.* Energy in the form of heat is removed from the liquid during the freezing process.

The amount of heat removed from a pure substance during freezing is characteristic of the substance. Thus 80 calories must be removed from 1 gram of water in order to change it from liquid to solid at 0°C . *The amount of heat which must be*

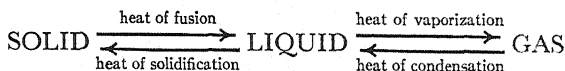
removed from a unit weight of substance in order to change it from liquid to solid is called the heat of solidification. It is usually measured in calories per gram.

The Kinetic Theory explains freezing. The molecules in a liquid move more rapidly and do not have fixed positions as they do in a solid. In order to slow the molecules, it is necessary to remove energy from them.

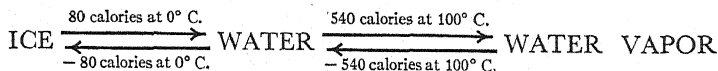
Melting

Melting is the reverse of freezing, for here a solid changes to a liquid. The phenomenon is sometimes called *fusion*. The temperature at which an equilibrium exists between solid and liquid is called *melting point*. For pure substances this is usually "sharp" — at a definite temperature — whereas for mixtures it occurs over a wide range, the solid thus slowly softening and then melting. It can be observed that ice melts at 0°C. , whereas fats, which are mixtures, melt over a wide range.

The heat of fusion is the amount of heat which must be added to a unit weight of substance to change it from a solid to a liquid. This too is usually measured in calories per gram. For water, it is 80 calories per gram.



For water, we have:



Specific Heat

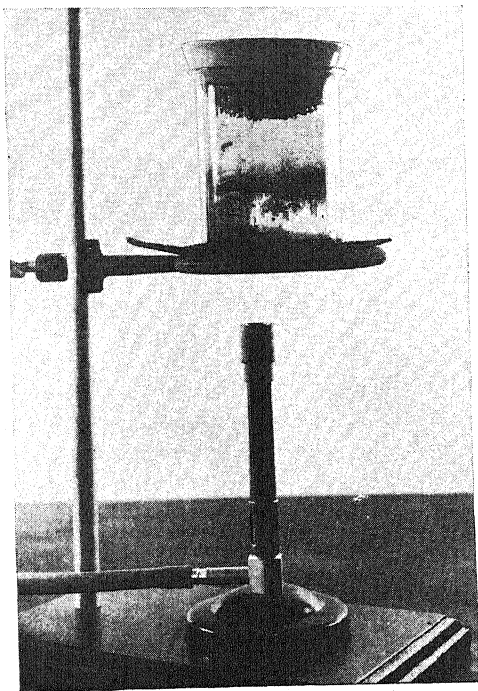
The amount of heat necessary to raise the temperature of 1 gram of substance 1 degree centigrade is called the *specific heat*. This varies with the substance, with its state, and to a certain extent with the temperature at which it is measured. For example at 20°C. , the specific heat of water is 1 calorie per gram while that of iron is only 0.1065 calorie per gram. Daily experience demonstrates this qualitatively. You know that if you place a toasting fork (it is not pure iron, but is similar to it) into a fire, the metal very quickly heats to a temperature which will burn you, but the wood handle does not. The specific heat of ice at -10°C. is

0.48 calorie per gram. The specific heat of water shows some variation over the range from 0° to 100° C., but it is slight (lowest 0.99743 calorie per gram at 35° C.; highest 1.00645 calories per gram at 100° C.).

Sublimation

A few solids show the property of sublimation. *Sublimation is the transition of a solid directly to a gas and back to a solid.* Moth crystals, either naphthalene or para-dichlorobenzene, do this when they vaporize and redeposit on your clothes. Actually most solids have some vapor pressure and therefore do sublime. Usually the term is applied to solids which show this to a marked degree. They are the solids with high vapor pressures. The process may be very well demonstrated by placing a mixture of sand and iodine in a beaker. An evaporating dish filled with cold water is placed on top of the beaker. On gentle heating, the purple vapors rise through the beaker, and black crystals of iodine form on the bottom of the evaporating dish. The sand shows no discernible tendency to sublime.

Fig. 7-21. Sublimation of iodine. Iodine changes directly from a solid to a gas on heating. When the gas comes in contact with a cool surface, it solidifies. Here iodine has been heated in the bottom of the beaker. The evaporating dish is kept cool by the water which it contains. Long needles of iodine have grown on the dish and some iodine is condensed on the sides of the beaker.



Applications

There are many applications of the transitions of states of matter in daily life. A few have been mentioned and a few more will be described. There are a number of examples of the cooling effect of evaporating liquids. Frequently farm women cool milk in pans of water with large surfaces. The coldness of the water will bring about some cooling, but the evaporation of the water will keep the temperature of the water below room temperature and will preserve the milk for short periods better than if it were at room temperature. Water bags are used in dry areas, such as the desert, where the rate of evaporation is fairly high and the cooling effect therefore marked. These water bags are composed

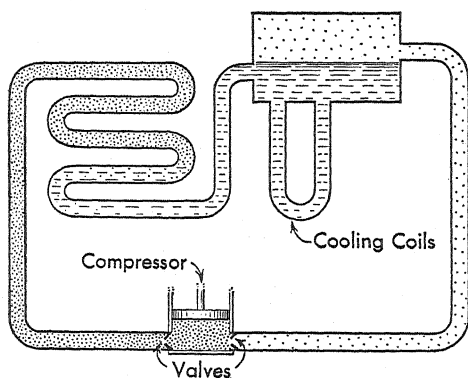


Fig. 7-22. Diagram of an automatic refrigerator. The cooling coils surround the freezing compartment. They are cold because of the rapid evaporation of the refrigerant in them. The gas formed on evaporation flows to the compressor where the pressure on it is increased until it liquefies.

of canvas. The fibers are wet with water and hence present a large area for evaporation.

A mechanical refrigerator is an example of cooling by evaporation. All mechanical refrigerators consist of a mechanism for compressing a gas and changing it into a liquid and then allowing that liquid to expand suddenly. The expansion chamber is the coils of the refrigerator or the plates. Figure 7-22 shows an example of one type of refrigerator. Here an electric motor compresses the gas in the coils until it changes to a liquid. The liquid passes through a needle valve into the cooling coils, where it is allowed to evaporate at low pressures. The dial which regulates the temperature of the cooling coils actually regulates the pressure at which the liquid evaporates. When a lower temperature is desired the compressor removes the gas formed from the cooling

coil chamber more rapidly. The food and refrigerator chamber supply the heat energy to the liquid which evaporates. The compressor does work and removes this energy by changing the gas back into a liquid. The gases which are used in home refrigerators must have a high critical temperature so that they are readily liquefied. They must also be nontoxic and noncorrosive, since occasionally leaks may develop in the line. In early models sulfur dioxide or ammonia was used. They have a critical temperature of 157.2 and 132.4° C. Today halogenated hydrocarbons are most frequently used, a very common one is Freon, CCl_2F_2 .

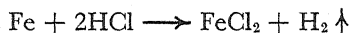
Pressure cookers are another example of an application of these generalizations on transitions in states of matter. A pressure cooker is arranged so that the pressure over the water in the cooker is increased by holding in the steam until it reaches pressures above atmospheric. Under the increased pressure, the boiling point of the water is raised since it takes a higher temperature to produce a pressure equal to that on the liquid. Pressure cookers are commonly operated at either 10 or 15 pounds pressure, occasionally at 5 pounds, above atmospheric. This represents a considerable increase in temperature of the boiling point of water. Solutions will have slightly different boiling points.

<i>Pressure</i>		<i>Boiling point of pure water</i>
<hr/>		
	(if atm. = 760 mm.)	
5 lb.	1018.5 mm.	108.4° C.
10	1277	115.2
15	1535.5	121

Pressure cookers are used in two ways, first to decrease the time of cooking and secondly to kill bacteria and molds. Since the rate of a chemical reaction roughly doubles with every ten-degree centigrade rise in temperature, the reaction rate at 121° C. is approximately four times as fast as at 100°. Cookery reactions are very complicated and not fully understood. This is a very rough approximation. Usually the cooking time is cut to one-third when 15 pounds pressure is used. Microorganisms are also killed much more rapidly at these higher temperatures.

GASES IN CHEMICAL REACTIONS*Weight-Volume Relations*

In Chapter 4 we studied the quantitative aspects of chemical reactions and learned that a chemical equation shows not only the number of molecules which are reacting and which are produced, but also the weights of compounds in *grams* (or pounds or any other weight units) which are reacting and which are produced. When one of the compounds is a gas, the equation tells us not only the weight of that gas which reacts but also the *volume under standard conditions*. One gram molecular weight of any gas occupies 22.4 liters at standard conditions, and if the balanced equation shows that one gram molecular weight of the gas is reacting or is produced, it also shows that 22.4 liters of that gas at standard conditions are involved in the reaction. For example,

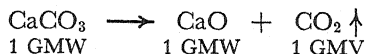


This equation tells us that one gram molecular weight of iron (55.85 grams) reacts with two gram molecular weights of hydrochloric acid (72.93 grams) to produce one gram molecular volume or *22.4 liters* at standard conditions of hydrogen. Since ferrous chloride, FeCl_2 , is a solid and not a gas, we cannot predict what its volume will be, but we do know from the equation that one gram molecular weight (126.76 grams) of ferrous chloride will be formed in the reaction.

We can now calculate the volumes of gases which will react or which will be formed if we know the weight of a reactant.

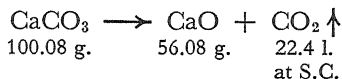
PROBLEM: Calculate the volume of carbon dioxide at standard conditions which will be formed from the complete decomposition of 5 grams of calcium carbonate.

ANSWER: The balanced equation for the reaction is:



This equation shows that one gram molecular weight of calcium carbonate decomposes to form one gram molecular weight of

calcium oxide and one gram molecular volume of carbon dioxide. In terms of weight and volume units, it tells us that:



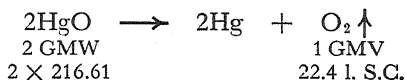
The volume of carbon dioxide produced from 5 grams of calcium carbonate will be in direct proportion to the 22.4 liters produced from 100.08 grams of calcium carbonate.

$$\begin{array}{l} \frac{5 \text{ g.}}{100.08 \text{ g.}} = \frac{x \text{ l.}}{22.4 \text{ l.}} \\ x = 1.12 \text{ l. of CO}_2 \text{ at S.C.} \end{array}$$

It is also possible to calculate the volume of a gas which will react or be produced at conditions of temperature and pressure other than standard. It is always necessary to compare volumes of gases under the same conditions and it is necessary, therefore, to use volumes of gases in these proportions at *standard conditions*. But if we know the volume of a gas at conditions other than standard, we can always calculate what the volume *would be* at standard conditions by use of the gas laws. Or if we find that a given volume of gas at standard conditions will be produced in a reaction, we can calculate later what the volume will be under different conditions.

PROBLEM: Calculate the volume of oxygen at 20° C. and 730 mm. pressure which will be produced when 10 grams of mercuric oxide completely decomposes.

ANSWER: Balanced equation:



Proportion:

$$\begin{array}{l} \frac{10 \text{ g.}}{2 \times 216.61} = \frac{x \text{ l.}}{22.4 \text{ l.}} \\ x = 0.52 \text{ l. at S.C.} \end{array}$$

We can now calculate what volume 0.52 liter at standard conditions will occupy at 20° C. and 730 millimeters pressure.

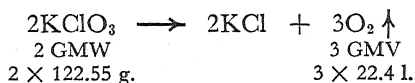
$$V = 0.52 \text{ l.} \times \frac{760}{730} \times \frac{293^\circ}{273^\circ} = 0.58 \text{ l. at 730 mm. and } 20^\circ \text{ C.}$$

PROBLEM: Calculate the amount of potassium chlorate which must be decomposed to form 100 milliliters of oxygen gas at 750 millimeters pressure and 15° C.

ANSWER: We must first calculate what volume the oxygen would occupy if it existed at standard conditions before we can compare the volume to 22.4 liters of gas at standard conditions.

$$V = 100 \text{ ml.} \times \frac{750}{760} \times \frac{273^\circ}{288^\circ} = 90.1 \text{ ml. or } 0.090 \text{ l. at S.C.}$$

Balanced equation:



Proportion:

$$\frac{x \text{ g.}}{2 \times 122.55 \text{ g.}} = \frac{0.090 \text{ l.}}{3 \times 22.4 \text{ l.}}$$

$$x = 0.33 \text{ g. of KClO}_3$$

NEW TERMS

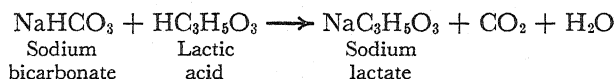
Barometer, diffusion, absolute zero, absolute scale, vapor pressure, standard conditions, aqueous tension, gram molecular volume, viscosity, surface tension, Van der Waals forces, condensation, evaporation, distillation, sublimation, fusion, critical temperature, critical pressure, heat of condensation, heat of vaporization, heat of fusion, heat of solidification, boiling point.

QUESTIONS

1. What characteristics make us recognize a gas, a liquid, and a solid as different states of matter?
2. What is diffusion? If a dense gas, such as chlorine, is released in a basement, will it rise through the house? How does the Kinetic Theory explain this?
3. What is a barometer? Why does it measure the pressure of the air? Why is air pressure always lower at high altitudes?
4. How does the Kinetic Theory explain the ability of gases to compress when the pressure on them is increased, while they expand when the pressure is decreased?
5. If a jar is capped tightly and placed in the oven, it will explode when the temperature of the air rises. How does the Kinetic Theory explain this observation?

6. What is viscosity? Some liquids have high viscosity at room temperature while others have high fluidity. How does the Kinetic Theory explain this? If you wish to test the jellying power of a pectin solution, you might use the viscosity as a measure. How would you measure this?
7. What is a crystal? Why do pure solids tend to form crystals?
8. What is a wetting agent? Why are wetting agents used in dyeing?
9. What is the surface tension of a liquid? How may it be decreased? Explain why a decrease in surface tension is desirable in washing fabrics.
10. A liter flask of oxygen is collected in the laboratory when the pressure is 740 mm. What would the volume have been for this quantity of gas if the pressure had been 750 mm.?
11. A bottle of hydrogen is collected over water in the laboratory when the pressure is 735 mm. and the temperature 20°C . What pressure is exerted by the water vapor? What pressure is exerted by the hydrogen? What volume would this quantity of hydrogen occupy if it were dried and held at a pressure of 760 mm.?
12. A balloon contains 1.5 liters of air at 740 mm. pressure and 18°C . If it is warmed to 40°C ., what volume will it have? If it is chilled to 0°C ., what will the volume be?
13. A bottle of air contains 450 ml. at 15°C . and 750 mm. pressure. What will the volume be if the temperature is decreased to 10°C . and the pressure increased to 800 mm.?
14. What is the absolute scale of temperature? Why is it necessary to use another temperature scale when there are already the Fahrenheit and the centigrade scales in use?
15. Calculate the volume which a quantity of chlorine will occupy at standard conditions if it fills a 250 ml. jar at 755 mm. pressure and 18°C ..?
16. To what temperature must 500 ml. of gas be cooled in order to decrease the volume by half without changing the pressure?
17. In the churning of a frozen dessert, it is always true that the rapid melting of the ice-salt mixture around the dessert is an indication of the freezing (solidifying). Explain.
18. Why does ice keep an icebox cool? Would solid carbon dioxide be more effective? Why?
19. A pot of tea (1000 cc.) is at 85°C . You wish to serve it cold at 3°C . How much ice will be needed to reduce the temperature? Neglect loss or gain of heat to the atmosphere.
20. How many calories of heat are absorbed in melting 10 g. of ice at 0° to water at 0° ?

21. On farms where there is no refrigerator or cold springs, farm women often keep milk for short periods by placing it in pans of water. Explain why this lowers the temperature.
22. Some crude air cooling systems are composed of wet cloths with an electric fan blowing air through them. Explain why this device should lower the temperature of the air.
23. In what way does the water content of the human body act to regulate the body temperature?
24. In what way does the passage of a current of air over a liquid hasten evaporation?
25. When a liquid has been heated to its boiling point, heat must be applied to continue the boiling. Why?
26. How many calories of heat would be absorbed in the melting of 1 lb. of ice at 0° to water at 0° ?
27. How many calories of heat would be absorbed in transforming 1 g. of ice at 0° into 1 g. of water vapor at 100° (assume that the specific heat of water is 1.0 over the range of 0° – 100°)?
28. A Dewar flask contains 1000 g. of water. The temperature of the water is 25° . To this is added 100 g. of ice of which the temperature is 0° . The flask is set aside until the temperature of the contents is constant. Calculate this temperature.
29. Calculate the volume of dry O_2 which will be produced at 25° and 750 mm. from 2.45 g. of $KClO_3$.
30. How much H_2O must be used to produce 250 ml. of dry O_2 at 15° and 740 mm.?
31. H_2 is produced by the action of 5 g. of Zn and HCl, and it is collected over water. If the temperature is 20° C. and the pressure is 737.5 mm., what is the volume of the wet gas?
32. Nitrogen and hydrogen react to form ammonia. Assuming completion, what volume of ammonia will be produced at 750 mm. and 15° C. if 2 liters of nitrogen at 750 mm. and 15° C. are used?
33. Baking soda reacts with the lactic acid of sour milk according to the following equation:



If 1 g. of baking soda is used in a recipe, what volume of carbon dioxide will be produced at an oven temperature of 175° C. and an atmospheric pressure of 740 mm.? Assume that the batter is perfectly elastic and that all of the soda reacts.

The Atomic Theory

The Atomic Theory is so useful in chemistry that many references have been made to the concept that matter is made up of atoms, combined in molecules, which undergo chemical reactions. It has been pointed out that there is sound reason to believe that matter is made up of particles. In order to account for the physical properties of matter the Kinetic Theory developed. The Atomic Theory explains many of the chemical properties of elements and compounds. Now this theory will be studied more carefully, and a brief survey of the internal structure of the atom and changes which may occur there will be included.

At the beginning of the nineteenth century Dalton, a poor English school teacher with an enormous curiosity about nature, began to work out an hypothesis to explain chemical reactions. By 1800, twenty-eight elements were known, but so active was the search at that time for the elements occurring in nature that in the next ten years fifteen more elements were discovered. It was a period in chemical research when the properties of these elements and their reactions were being vigorously

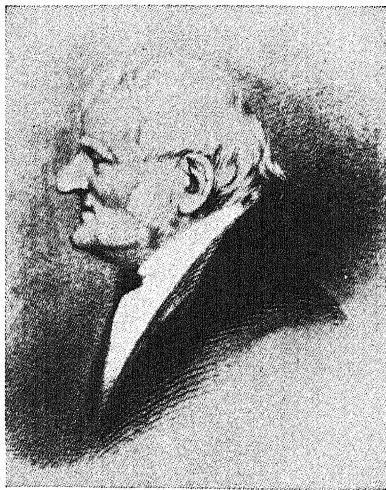


Fig. 8-1. John Dalton. (Courtesy of Journal of Chemical Education.)

studied. There was a need for a theory which would make the multitude of facts accumulating both comprehensible and coherent. Dalton supplied this hypothesis which grew eventually to be the Atomic Theory.

Dalton suggested that:

1. All atoms of the same element are alike.
2. The atoms of different elements are different.
3. Atoms are the particles which participate in chemical reactions.
4. Atoms are indivisible.
5. Molecules contain a definite number of atoms.

This hypothesis of Dalton was not entirely new. Democritus, one of the Greek philosophers, suggested that matter was made

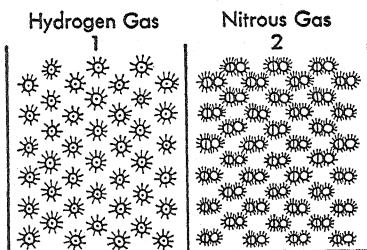


Fig. 8-2. Dalton's atoms. Dalton visualized "nitrous gas" as composed of atoms of nitrogen and oxygen held together in the ratio of one to one. (Roscoe and Hardin, *A New View of Dalton's Theory*, Macmillan and Company.)

up of hard, indivisible particles and he had coined the term "atoms" to apply to these particles. This hypothesis had been used occasionally by other men attempting to explain nature from that time until Dalton developed it into a working hypothesis. His assumption that atoms of one element were alike but different from atoms of another element led to the realization that the *weights* of atoms of different elements must be different. He began to try to determine the *relative* weights of different elements. During the nineteenth century, chemists developed the ideas of molecules and formulas and extended their knowledge of particular compounds. Atomic and molecular weights were determined with greater and greater accuracy and clearer insight into their significance. The atomic hypothesis became the Atomic Theory and chemistry emerged as a *quantitative science*.

At the end of the nineteenth century, the idea of the indivisibility of atoms received a shattering blow by the discovery of radioactivity. Becquerel, then the Curies, and later a larger number of other physicists and chemists observed that radio-

active elements disintegrate spontaneously and that the atoms of these elements are actually divisible. Today the Atomic Theory postulates that the atoms of all elements are composed of similar particles put together in varying arrangements. The atoms are composed of a nucleus which is positively charged, very compact and dense, around which rotate, far out in space, the electrons.

During the past fifty years atomic physicists have demonstrated the occurrence of a number of subatomic particles. These are particles which are smaller than atoms and which originate in them. Some are formed and then disappear very quickly. Only three will be considered, the proton, the neutron, and the electron, whose place in the atom is well understood. The Atomic Theory may be further modified with the accumulation of more knowledge about these particles.

Before World War I, Moseley, a young English physicist, devised a way to measure the atomic number of an element. *The atomic number of an element is the positive charge on the nucleus.* When an element is bombarded with fast electrons, it emits x-rays. Moseley discovered that the wavelength of these x-rays is characteristic of the element and can be used to calculate the charge on the nucleus. He did not have time to complete this important work because he lost his life on the battlefield, but others have made the measurements and applied his observations.

The Nucleus

Many observations in recent years have confirmed the early hypothesis of Rutherford that the atoms of all elements are remarkably porous. Rutherford bombarded very thin goldleaf

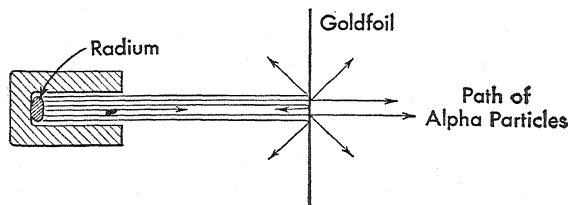


Fig. 8-3. Rutherford's experiment demonstrating the porosity of atoms of gold. Many alpha particles passed through the gold foil, some were deflected as they passed through the gold, and some bounced back off the gold without penetrating it.

with alpha particles. These are particles which are emitted by radium and, it is now known, are positively charged helium atoms. Rutherford did not know the nature of these particles, but he did know that they possess a positive charge and a small mass. He found that most alpha particles penetrated the goldfoil readily. Only one in every ten million was deflected. He therefore concluded that the gold atom was porous.

Physicists have now made sufficient measurements on atoms to estimate the approximate size of the nucleus in relation to the rest of the atom. The diameter of the nucleus is approximately one-ten thousandth the diameter of the atom. The size of the nucleus in the atom has been aptly likened to that of a fly in a cathedral.

This nucleus contains most of the mass of the atom and is, therefore, remarkably dense. It is composed of *protons* and

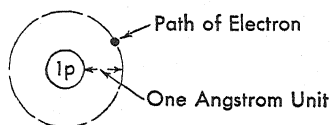


Fig. 8-4. Diagram of the hydrogen atom. The electron rotates around a nucleus composed of one proton. The size of the nucleus is greatly exaggerated in this diagram.

neutrons. The protons are ultimate particles of matter which have a charge equal to that of the electron, but opposite in sign. Therefore the proton has a positive one charge compared to the electron as minus one. The mass of the proton is approximately equal to that of the hydrogen atom ($^{1845}/_{1846}$ of it) and, therefore, on the atomic weight scale the proton has a mass of one.

Neutrons are neutral particles which have neither a positive nor a negative charge. Their mass is equal to that of the proton, or is one on the atomic weight scale. The nucleus, then, has a mass equal to the number of protons and neutrons present in it and a positive charge equal to the number of protons.

Electrons

In 1913 Bohr suggested the orbital theory of the atom and with slight modifications it is most useful in explaining chemical properties of elements. According to this theory the electrons rotate at very high speed around the positively charged nucleus and thereby give the atom a kind of three-dimensional size. Thus hydrogen, the lightest element, is composed of one proton

in the nucleus and one electron rotating around it rapidly. This electron moves rapidly in the space about one Angstrom unit (0.0000001 mm.) from the nucleus and gives the atom a diameter of two Angstrom units.

Ultimate Particles of Matter			
Place	Particle	Charge	Mass on atomic weight scale
Nucleus	Protons	+1	1
	Neutrons	0	1
Outside nucleus	Electrons	-1	1
			1846

Isotopes and Atomic Weights

The atomic weights of most elements are not whole numbers although many of them are close to it. Carbon is 12.01, calcium is 40.08, nitrogen is 14.01. If the mass of the atom is contained primarily in the nucleus and if this nucleus is made up of protons and neutrons each with a mass of one, it would be expected that the atomic weights should be very close to whole numbers. At first glance it appears that the Atomic Theory does not fit the facts very well. However, it is now known why it is that atomic weights are fractional. The atoms of one element are not all equal in weight. Dalton's original assumption is true to only a limited extent.

It has been demonstrated that all elements are composed of two or three different kinds of atoms. These atoms are identical in all respects except the atomic weight. They are called *isotopes*. *Isotopes are atoms of the same element which differ in atomic weight but which have the same atomic number.* The atomic number is equal to the charge on the nucleus, and these isotopes therefore have the same charge on the nucleus. Thus all samples of chlorine are made up of some atoms with a mass of 35 (76%) and some with a mass of 37 (24%), while all samples of neon contain some atoms with a mass of 20, some of 21, and some of 22.

Keeping in mind the occurrence of isotopes, a very clear picture of the structure of the atoms can be drawn. The nucleus of the atom of any element is composed of protons and neutrons and the total number is equal to the mass of that atom. Since one isotope usually has a mass equal to the rounded off number of the average atomic weight, this rounded off number may be

used in the picture. The number of protons is equal to the atomic number. The number of neutrons is equal to the difference between the atomic weight and the atomic number. Thus the nuclei listed are constructed as follows:

	<i>Helium</i>	<i>Lithium</i>	<i>Beryllium</i>
Atomic weight	4.003	6.940	9.02
Atomic number	2	3	4
Number of protons	2	3	4
Number of neutrons	2	4	5

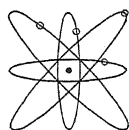
In a free uncombined element, the number of electrons is equal to the number of protons in the nucleus and therefore to the atomic number. Thus helium has two electrons rotating rapidly around the nucleus far out in space, whereas lithium has three, and beryllium four.

Electron Orbits

The electrons rotate at fixed distances from the nucleus of an atom. Those electrons which are approximately the same distance from the nucleus are said to occur in the same "shell" or "ring." In elements which have large numbers of electrons these shells contain the following number of electrons:

Shell 1 ("k level")	2
Shell 2 ("l level")	8
Shell 3 ("m level")	18
Shell 4 ("n level")	32

The shells are often designated "k," "l," "m," etc., instead of "1," "2," "3." This designation arose from the fact that the German word for "short" is "kurt" and this shell has the smallest number of electrons. However, an element never contains more



or Schematically

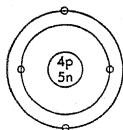


Fig. 8-5. *Beryllium atom.*

than 8 electrons in its outer shell. If the element has a small number of electrons, they are still arranged according to this pattern. Thus beryllium has four electrons, two in the first shell and two in the second shell. Neon has ten electrons, two in the

first shell and eight in the second; potassium has nineteen electrons, two in the first shell, eight in the second, eight in the third, and one in the fourth. These electrons are pictured as rotating at high speed in orbits around the nucleus. Bohr's diagram of the free beryllium atom would be as in Fig. 8-5. The schematic picture of the beryllium atom on the right indicates by the circles around the nucleus, the electron shells and the number of electrons which occur in these shells. The diagram does not indicate the correct distance of the shell from the nucleus or the various orbits in three-dimensional space which the electrons describe. To try and represent this would take a very large

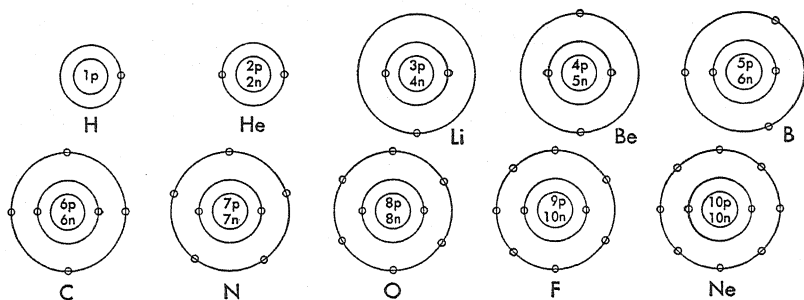


Fig. 8-6. Diagrams of the structures of the first ten atoms.

sheet of paper, and the projected orbits for the heavier elements which have a large number of electrons, would look like a snarl.

Valence

In the early nineteenth century an attempt was made to explain the nature of valence or the chemical bond. What is it, chemists asked, which holds atoms together in molecules? It was known at that time that when solutions of many compounds are placed in an electrolytic cell, part of the molecule migrates to the positive electrode and part to the negative electrode. Thus in potassium chloride solution, the potassium migrates to the negative electrode and thereby demonstrates its positive charge, while the chlorine migrates to the positive electrode and must therefore be negative. At that time, it appeared as if the nature of the chemical bond were electrical. Later a number of compounds were observed in which there was no migration in an electric field. When the atomic theory was developed, it was

necessary to account for the occurrence of molecules which had strong positive and negative charges in them and for some which had none or very little charge.

Of all the elements which are known to chemistry, only the rare gases, helium, neon, argon, krypton, xenon, and radon are inert chemically. They do not combine with other elements to form compounds. They exist as single atoms in each molecule. These elements have eight electrons in the outer shell with the exception of helium, which has two in its outer orbit (an only orbit).

On the basis of the observation on inert gases and the demonstration of the charge on some elements in compounds, the Octet Theory postulates that when atoms combine there is a tendency for them to possess eight electrons in the outer shell. Very light-weight elements will possess two. An element which

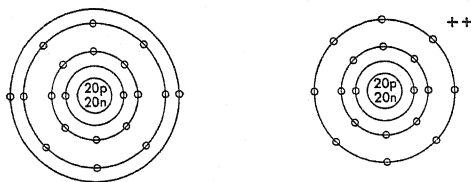


Fig. 8-7. Diagrams of the calcium atom and calcium ion.

has an arrangement of electrons of 2, 8, 8, 1 (potassium) will combine with another element by losing its outer electron. It will then have an arrangement of electrons of 2, 8, 8, and since the charge on the nucleus is $+19$ and the number of electrons is now 18 with a charge of -18 , the atom residue will have a $+1$ charge. This will be the *potassium ion*. Calcium, with an arrangement of electrons of 2, 8, 8, 2, will on combination lose two electrons, and since the nucleus is charged $+20$ and there are then only 18 electrons arranged 2, 8, 8, the *ion* will possess a charge of $+2$.

What happens to the electrons which are lost by potassium or calcium or any element containing one, two, or three electrons? These elements commonly combine with elements which possess in their outer shells six or seven electrons. Now, an element which contains six or seven electrons in its outer shell tends to gain electrons to form eight, when it combines. Free fluorine possesses nine electrons arranged 2, 7. When it combines, it gains

one electron to form the fluorine ion with an arrangement of 2, 8 electrons. Since the fluorine nucleus has a charge of $+9$ and since there are now 10 electrons rotating about this nucleus, the charge will be -1 . This is the *ion* of fluorine. If the fluorine

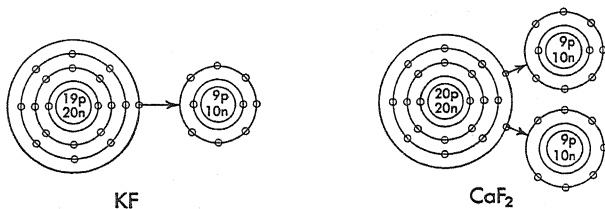


Fig. 8-8. Diagram of electrovalent compounds. The single headed arrow indicates that when combination takes place, the electron is lost to the other atom.

combines with potassium to form potassium fluoride, the fluorine will gain the electron which the potassium atom loses. If it combines with calcium, *two* fluorine atoms will each gain one electron of the two lost by *one* calcium atom. Thus there are molecules with the composition of one potassium and one fluorine, KF or molecules containing one calcium and two fluorines, CaF₂. This type of combination is called electrovalence. *Electrovalence is the type of chemical combination in which electrons are gained or lost.*

Atoms which possess four or five electrons in their outer orbits show little tendency to form molecules in which positive and negative charges are present, unless their atomic weights are

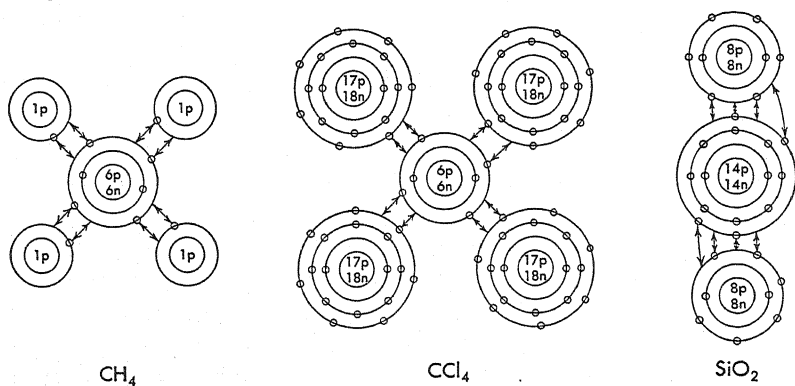


Fig. 8-9. Diagrams of covalent compounds. Double headed arrows are used to indicate the sharing of electrons.

high. Thus carbon possesses six electrons, arranged 2, 4, but most of its compounds do not have positive or negative charges present (they are not ions). Instead, the electrons are only partially lost — they are shared with the other element and they begin to rotate around both nuclei. In the compound of carbon and hydrogen, methane, CH_4 , the carbon shares one of its electrons with each hydrogen and each hydrogen shares its electron with the carbon. Thus the carbon has eight electrons rotating in its outer shell, four of its own and one from each of the four hydrogen atoms. Each hydrogen has two electrons rotating in its shell, one of its own and one from the carbon. There are only eight electrons involved here, but because they are shared and rotate rapidly around each nucleus, the carbon has eight different electrons, and the hydrogens each have two. This type of combination is called covalence. *Covalence is the type of chemical combination in which there is a sharing of electrons.*

Summary

1. Elements which possess one, two, or three electrons in their outer shells tend to lose these electrons, when they combine with other elements.
2. Elements which possess six or seven electrons in their outer shell tend to gain two or one electrons to make up eight, when they combine chemically.
3. Elements which possess four or five electrons in their outer shell tend to share electrons with the elements with which they combine to form eight in each outer shell.
4. Elements which possess eight electrons in their outer shell do not combine.

Another type of valence is coordinate covalence. In this type of combination electrons from one atom are shared with another atom which does not contribute any to the sharing. It is a one way sharing. Thus when ammonia reacts with hydrochloric acid to form ammonium chloride, this type of valence accounts for the bond. Ammonia is a covalent compound in which nitrogen shares three of its five outer electrons with the three hydrogens, and the three hydrogens share their electrons with the nitrogen. This nitrogen then has eight electrons rotating in the outer shell, five of its own and three from the hydrogens.

Each hydrogen has two electrons, one of its own and one from the nitrogen. Of the five electrons which the nitrogen possessed in its outer shell when it was free, three are shared with hydrogens. In solution hydrochloric acid is an electrovalent com-

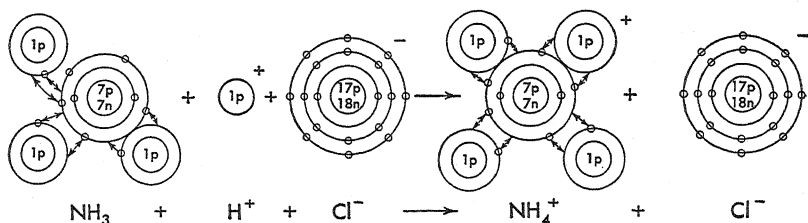


Fig. 8-10. Diagram of the formation of coordinate covalence. The hydrogen ion of the HCl moves up to the nitrogen and begins to share two of its electrons.

pound in which the electron from the hydrogen is lost to the chlorine. The chlorine then has eight electrons in its outer shell, seven of its own and one from the hydrogen. The hydrogen has no electrons. When these two compounds, ammonia and hydrochloric acid, react, the hydrogen ion which has no electrons, begins to share the two unshared electrons rotating about the

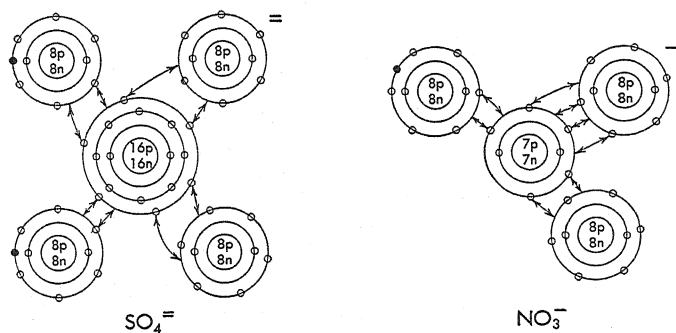


Fig. 8-11. Diagrams of the sulfate and nitrate ions. Both have covalent bonds and coordinate covalence bonds. The electrons on two sulfate oxygens and one nitrate oxygen which are black, are derived from the positive ions.

nitrogen. The bond between this hydrogen and the nitrogen is a coordinate covalent bond.

Radicals are held together by covalent and coordinate covalent bonds. Frequently both bonds will be present. In the

sulfate radical, SO_4^- , there are covalent bonds between the sulfur and two of the oxygens and coordinate covalent bonds between the sulfur and the other two oxygens. The dots indicate the electrons originally in the outer shell of the sulfur, the crosses those originally present in the outer shells of the oxygen atoms, and the circles the electrons lost by the cation (hydrogen, sodium, or whatever it may be) to sulfate. In nitrate, there are covalent bonds between the nitrogen and two of the oxygens.

One is a single bond with the sharing of two electrons, one from each atom, and one is a double bond with the sharing of four electrons, two from each atom. The third atom of oxygen is held to the nitrogen by a coordinate covalent bond.

Variable valence may be accounted for by a difference in the arrangement of electrons. Iron has an atomic number of 26, and therefore possesses 26 electrons in the free state. When it combines to form ferrous compounds, the iron loses two electrons and the arrangement of electrons is then 2, 8, 14 with a charge of positive two on the ion. When it combines to form ferric compounds, the iron loses three electrons and then has an arrangement of 2, 8, 13.

The chemical identity of isotopes is readily understood on the basis of the theory. Chlorine, you will remember, has two isotopes, chlorine 35 and chlorine 37. The atomic number of the element is 17 and there are therefore 17 electrons *for each isotope*. They are arranged in each isotope, 2, 8, 7. Each will tend in chemical combination, to gain one electron. The difference between the isotopes is in the number of neutrons present in the nucleus. Chlorine 35 has 18 neutrons, while chlorine 37 has 20.

RADIOACTIVITY

The discovery of radioactivity in the last decade of the nineteenth century provided the impetus for the development of the Atomic Theory. The knowledge of the particles which make up the nucleus of the atom, developed through a study of the emanations of radioactive material.

History

Becquerel, a physicist at the Sorbonne in Paris, observed in 1896 that some minerals were capable of producing a spot on a photographic film which is similar to that produced by light. These minerals appeared through this action to be giving off *radiations*. No matter how carefully the film was wrapped in paper, when he placed the mineral on it and developed the film, an image of the mineral appeared on it. Becquerel found that this property was present in salts of uranium and its minerals. He also observed that the air becomes ionized in the vicinity of these minerals and that an electroscope is discharged.

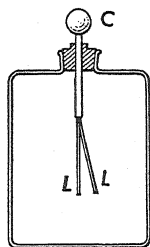


Fig. 8-12. Electroscope. The leaves, L, bear a like charge and therefore repel one another.

An electroscope is a device which consists of a metal conductor *C*, attached to two gold leaves, *L*, contained in a box. When an electric charge is placed on the conductor ball, it is transmitted to the leaves, and they attain the same charge. Since like charges repel, the leaves separate and stand out from one another. If the charge is withdrawn from the electroscope by contact with a body which can accept a charge, the leaves lose their charge and fall together. Or if the charge is neutralized by contact of the conductor with a body bearing a different charge, the charge on the leaves is neutralized and they fall together. Ordinarily the leaves will retain their charge for a fair length of time, since air is a poor conductor and acts as an insulator. When air is ionized, however, the charge is rapidly lost by the electroscope and the leaves fall. An electroscope may be used for detecting the presence of radioactive material by rapidly discharging.

At the time when Becquerel was studying this interesting phenomenon, a young Polish girl, Marie Sklodovska Curie was searching for a doctorate problem in Physics. She and her

husband, Pierre Curie, a physicist, were fascinated by Becquerel's work. She decided to study the nature of what she named radioactivity. She discovered that the wastes from pitchblende, a uranium mineral, contained more radioactivity than uranium salts. In the long search to account for this radioactivity, she was joined by Pierre Curie. Eventually they isolated two new elements, polonium and radium.

Rutherford, an English physicist, was very interested in the discoveries of the Curies. He studied the emanations from the radioactive elements and was able to demonstrate that there were three types of "particles" or "rays" thrown off. He accomplished this by inserting a small amount of radioactive material in the bottom of a thick lead tube. The lead screened out all radiations except those which escaped up the tube. Above the tube, Rutherford placed a magnet and above this a film. Three spots showed on the developed film, indicating that one type was attracted to the negative pole, one type of radiation was attracted slightly to the positive pole and one type of ray was not influenced by the magnet. Rutherford called these rays alpha rays (α), beta rays (β), and gamma rays (γ). Later it was shown that alpha rays are ions of helium, each bearing a plus two charge. Beta rays are electrons, while gamma rays are radiant energy rays with wavelengths similar to that of x-rays, but somewhat shorter.

Radioactive Emanations

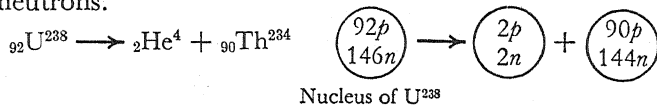
<i>Name</i>	<i>Nature</i>	<i>Attracted to</i>
Alpha rays	Helium ions ⁺⁺	Negative pole
Beta rays	Electrons (-1)	Positive pole
Gamma rays	Radiant energy rays	Neither pole

These particles are shot out at high speed and consequently have a high penetrating power. The alpha particles can penetrate only very thin sheets of metal, probably because of the relatively great size of the ions. They may be screened out by paper. Beta particles are able to penetrate gold leaf and similar thin sheets of metal, while gamma rays show very high penetrating power. They can penetrate one foot of steel or two inches of lead. The relative penetrating power of these rays is approximately in the ratio of 1:100:10,000 for alpha, beta, and gamma rays.

What Is Radioactivity?

The nature of radioactivity was explained in 1903 by the theory of Rutherford and Soddy. They postulated that radioactive elements are elements which disintegrate spontaneously to produce radioactive rays, a simpler element and heat. Since that time this theory has been widely accepted and expanded.

Today radioactivity is understood to be a spontaneous disintegration of the nucleus of heavy elements. The radioactive rays thrown off are characteristic of the element. Thus uranium 238 gives off alpha particles while thorium 234 gives off beta particles. The disintegration of a nucleus is accompanied by a loss of energy. This energy is in the form of heat and frequently gamma rays. When uranium 238 loses an alpha particle it is losing two protons and two neutrons. Since the nucleus of uranium 238 contains 92 protons and 146 neutrons, the newly formed element will have a nucleus made up of 90 protons and 144 neutrons.

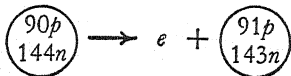


This element will have an atomic number of 90 and an atomic weight of 234. This atom will then be thorium 234.

The loss of a beta particle is the loss of an electron. But, you will remember, no electrons were postulated in the nuclei of atoms. Physicists have demonstrated that the probability of the presence of a negatively charged particle in the nucleus of any atom is extremely remote. The assumption of the theory is that the electrons emitted by radioactive atoms arise through the disintegration of a neutron into a proton and an electron.



When thorium 234 emits an electron it will then produce a nucleus which has one more proton and one less neutron than the original nucleus. The nucleus composed of 90 protons and 144 neutrons now becomes a nucleus composed of 91 protons and 143 neutrons. This is an atom with an atomic number of 91 and an atomic weight of 234. It is therefore protactinium 234.



Since electrons are available or easily sloughed off, the electrical balance of these particles is readily adjusted. The plus two helium ions soon pick up two electrons from the environment and become helium atoms with a zero charge. The newly formed thorium atom readily loses two orbit electrons to the environment. Notice that these electrons are not beta rays. Beta rays are shot out of the nucleus with a speed of 100,000 miles per second. These orbit electrons are simply sloughed off.

Radioactive Series

You have probably anticipated that radioactivity, then, gives rise to a *series* of disintegrations. Uranium disintegrates to form thorium; thorium disintegrates to form protactinium; protactinium forms uranium again and this forms thorium, then radium. The series continues, one element giving rise to another until finally a stable atom is formed. The stable atoms are lead. They do not disintegrate and the series therefore stops with them. A pure compound of any of the radioactive elements soon becomes a mixture and therefore gives off all three types

TABLE OF URANIUM SERIES *

Name	Symbol	Atomic Weight	Atomic Number	Isotope	Radiation	Half Life
Uranium I	UI	238	92	U	α	4.67×10^9 yr.
Uranium X ₁	UX ₁	234	90	Th	β	24.6 days
Uranium X ₂	UX ₂	234	91	Pa	$\beta(\gamma)$	1.15 min.
Uranium II	UII	234	92	U	α	2×10^6 yr.
Ionium	Io	230	90	Th	α	6.9×10^4 yr.
Radium	Ra	226	88	Ra	$\alpha(\beta + \gamma)$	1690 yr.
Radon	Rn	222	86	Rn	α	3.85 days
Radium A	RaA	218	84	Po	α	3 min.
Radium B	RaB	214	82	Pb	$\beta(\gamma)$	26.8 min.
Radium C	RaC	214	83	Bi	β	19.5 min.
Radium C'	RaC'	214	84	Po	α	10^{-6} sec.
Radium D	RaD	210	82	Pb	β, γ	16.5 yr.
Radium E	RaE	210	83	Bi	β	5 days
Radium F	RaF	210	84	Po	$\alpha(\gamma)$	136 days
Radium G (lead)	RaG	206	82	Pb		Infinite

* McPherson, Henderson, Fernelius, and Mack, *Chemistry: A Textbook for Colleges*, p. 223. Copyright 1940, by Ginn and Company and used with their permission.

of rays. In nature, there are three disintegration series — one starting with uranium 238, one with thorium, and one with uranium 235. All disintegrate through various isotopes of intermediate elements to a stable isotope of lead.

Half-Life Period

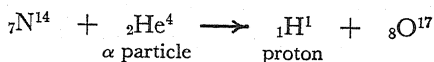
The rate at which a radioactive element disintegrates depends on the concentration of the element present and the nature of the element. The rate is not affected by heat or pressure and cannot be catalyzed. Some radioactive elements disintegrate rapidly, others very slowly. For example, one-half of a sample of uranium 238 will disintegrate in 4.67×10^9 years, while half of a sample of polonium 214 will disintegrate in 0.000001 second. The amount of disintegration depends on the amount of the element present. One gram of uranium 238 will produce half a gram of thorium in 4.67×10^9 years, and if it were possible to collect a ton of uranium it would produce a half ton of thorium in that length of time. In the next 4.67×10^9 year period, the remaining half gram of uranium will produce one-fourth gram. After an infinite length of time, there will still be a small amount of uranium left. The rate of disintegration of a radioactive element is therefore measured in terms of the *half-life period*. The half-life period is the length of time necessary for the radioactive disintegration of half of a sample of an element.

Radium Clock

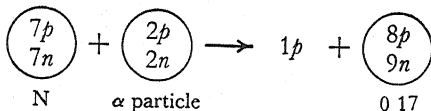
Minerals which contain radioactive elements furnish scientists with a rough kind of clock to measure the age of the world. If a mineral contains uranium, radium, helium, and lead, it may be assumed that all the helium has been produced by radioactive disintegration and that some of the helium produced has escaped. It may also be assumed that probably all of the radium has been produced by radioactive disintegration of uranium and its products, and that the lead may also have been formed in this manner. If the proportion of these four elements is determined, and the rate of disintegration is known, it is possible to calculate the minimum and the maximum time that the sample has been decomposing. This will give the minimum age of the world. From calculations of these factors it appears that the minimum age of the world is 1,000,000,000 to 1,500,000,000 years — such a long time that it is difficult for our finite minds to grasp.

Artificial Radioactivity – Nuclear Reactions

In 1919 Rutherford investigated the effect of alpha particles on the elements, particularly light-weight elements. He found that occasionally an alpha particle penetrated the orbit electrons and collided with the nucleus of an atom. The astounding result of this collision was the production of a different element. Rutherford on a minute scale had achieved the *transmutation of elements*. Radioactive elements undergo a spontaneous natural transmutation to another element but this was a man-made transmutation. If the nucleus of a nitrogen atom and an alpha particle collided, he had evidence that a proton was knocked out and an oxygen 17 atom formed.



Or a diagram of the nuclei involved:



This is no chemical reaction, but a *nuclear reaction*.

You may well ask how it was possible to detect the collision of two particles as minute as an atom of nitrogen and an alpha particle. The Wilson cloud chamber is the answer. When ions are formed in air super-

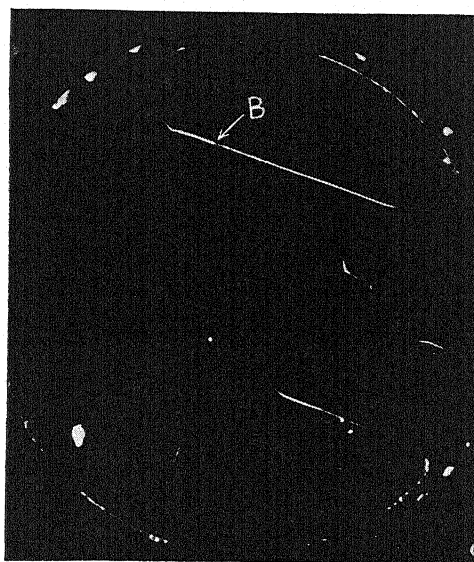
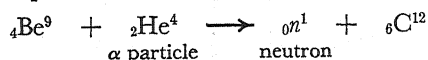


Fig. 8-13. Nuclear reaction shown by fog track in a Wilson cloud chamber. This is a reaction of helium 3 with a neutron to form a proton and hydrogen 3. Point B shows the break in the track. (Courtesy of Argonne National Laboratory.)

saturated with water, tiny droplets precipitate around each ion and a fog tract is produced. The rapid passage of an alpha particle through air causes the loss of electrons from some atoms and the gain by others. In other words the air is ionized. The path of the alpha particle is shown by the fog tract and if the alpha particle collides with an atom, this too can be seen.

Rutherford demonstrated nuclear reactions between atoms of most light elements and alpha particles.

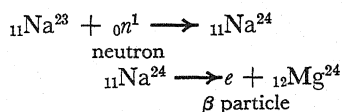
In 1932 Chadwick discovered neutrons while he was studying these nuclear reactions. He found that occasionally the collision of an alpha particle and the nucleus of beryllium or boron produced a neutral particle. This particle was a neutron.



There have been a large number of studies of nuclear reactions in the past twenty years. Other particles such as protons and deuterons (a heavy hydrogen ion) have been used. They are sped up by use of a cyclotron and at these enormous speeds have a greater chance of colliding with nuclei of other atoms.

In 1934 the Curie-Joliot discovered that after a nuclear reaction the newly produced atom was sometimes radioactive. Thus, they had produced a radioactive element. This is called *artificial radioactivity* since it is man made.

EXAMPLE:

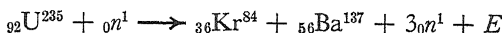


Finally Hahn and Strassmann found that the collision of a slow neutron with uranium

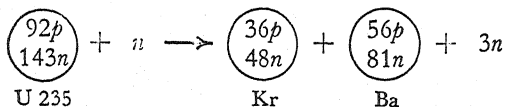


Fig. 8-14. Lise Meitner, physicist.
(Courtesy of World Wide Photos.)

235 resulted in the production of two middle-weight atoms, such as krypton and barium, several neutrons, and a great deal of energy. Lise Meitner calculated the energy relations.



If the nuclei involved in this reaction are diagrammed you will see that some matter disappears. The products are variable (thirty different elements have been identified), and the use of three neutrons per molecule of uranium hit is an approximation.



There are 92 protons on each side of the reaction, but there are 144 neutrons on the left-hand side and 132 on the right-hand side. If this equation is correct, 12 neutrons have disappeared. This type of nuclear reaction is called *fission*. *Fission is the disintegration of a nucleus into two middle-weight atoms.* It is accompanied by the release of a large amount of energy.

Almost forty years ago Einstein worked out the mathematical relation of matter and energy

$$E = mc^2$$

where E is ergs of energy, m is grams of matter and c the speed of light in centimeters per second. Since c is a large number the amount of energy produced from 1 gram of matter is enormous.

$E = m \times 9 \times 10^{20}$. The great source of energy to be found in atoms has been told over and over. It is the energy released on fission to which these journalists refer. It has been

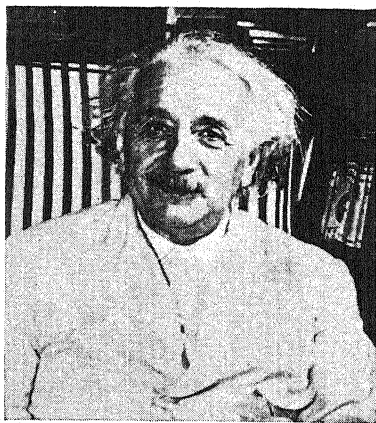
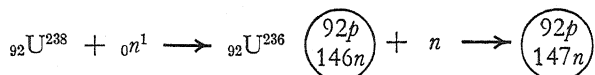


Fig. 8-15. Albert Einstein. (Courtesy of World Wide Photos.)

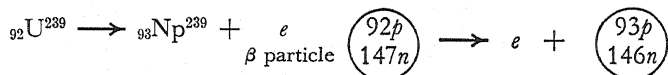
calculated that if 1 pound of matter were to be changed into energy, it would yield the equivalent of 11.4 million kilowatt-hours. In my home I use about 1500 kilowatt-hours in a year. If that pound of matter could be efficiently transformed into electric energy, there would be enough to run my home 10,000 years.

New Elements

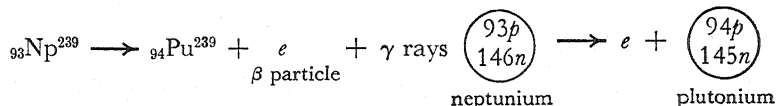
The studies of nuclear reactions and the development of the atomic bomb, has resulted in the preparation of six new elements with atomic numbers higher than uranium. The bombardment of uranium 238 with neutrons terminates in some capture reactions with the production of a new uranium isotope, uranium 239.



This isotope has a short half-life period of 23 minutes and rapidly disintegrates with the emission of beta rays. It thereby produces an element with 93 protons. This element has been named neptunium, Np.

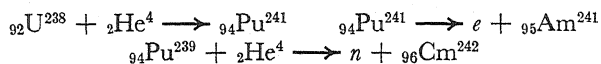


Neptunium is an element which has never before been detected, and so far the search for it in radioactive minerals has been fruitless. It is another radioactive element as are all the very heavy elements, and its half-life period is just 2.3 days. Since it has such a short half-life period, it is not surprising that the element has not been detected in radioactive elements. The radioactive disintegration of neptunium results in beta rays and another new element, plutonium, Pu.



Plutonium is an element which like uranium 235 undergoes fission when it is struck by slow neutrons. Of the two atom bombs dropped in 1945, one was the fission of uranium 235 and

one was the fission of plutonium. Two other elements, americium which has atomic number 95 and curium which has atomic number 96, have been prepared by bombardment of uranium 238 and plutonium 239 with speeded-up alpha particles. Element 97 is called berkelium and element 98 is californium.



A more stable isotope of neptunium has also been detected. It is neptunium 237 and has a half-life period of 2.25×10^6 years.

Use of Isotopes in Biochemical Studies

Isotopes are chemically indistinguishable from one another, and they are therefore useful in tagging molecules and making it possible to trace these molecules through the complex reactions which occur in cells. In a cell, a number of reactions occur simultaneously, and it is exceedingly difficult to trace the course of each reaction. Some of the isotopes of elements which com-

monly occur in compounds which are used and produced by cells may be readily distinguished and thereby tag the molecules to which they are attached. The cell uses these molecules in the same reactions in which it would use normal molecules. The isotopes which are most easily used are deuterium ("heavy hydrogen"), nitrogen 15, and radioactive elements.

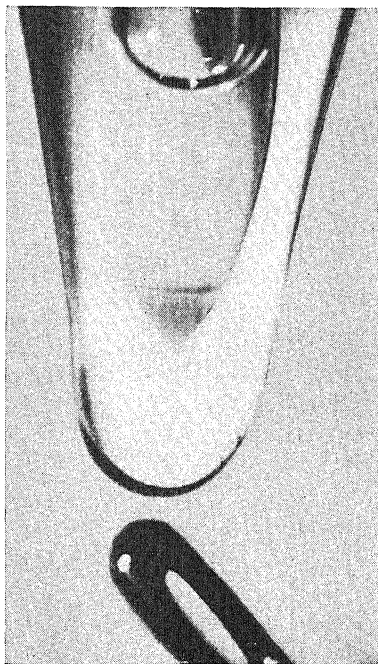


Fig. 8-16. First sample of pure americium compound compared to the eye of a needle. (Courtesy of Dr. Glenn T. Seaborg.)

Deuterium is the special name applied to hydrogen with an atomic weight of two. This isotope merits a special name because its physical properties are slightly different from those of hydrogen one or of the mixture of hydrogen one and two which occurs all over the earth. When you generate hydrogen in the laboratory from hydrochloric acid and zinc, or when you electrolyze water, you produce in the molecules of hydrogen a mixture of atoms with a ratio of approximately 6000 atoms of hydrogen one to one atom of hydrogen two. You will remember that we learned, when isotopes were described, that with one or two exceptions there is a constant ratio of the isotopes in various samples of all elements no matter what their source. The nucleus of hydrogen one contains one proton and *no* neutrons, while the nucleus of hydrogen two contains one proton and *one* neutron. There is a 100 per cent difference in the atomic weights of these isotopes and consequently their densities are slightly different. Most isotopes contain such heavy nuclei that a difference of one neutron in the nucleus does not alter the atomic weight by such a proportionally great amount, and the physical properties of these isotopes are not measurably different. But in the isotopes of hydrogen there is a proportionally great difference in atomic weight and this is reflected in the physical properties of the two isotopes. Ordinary water has a density of 1.00000 gram per milliliter at 4° C., while water in which the hydrogen is the deuterium isotope, D_2O or heavy water, has a density of 1.1079 grams per milliliter.

Deuterium has been used to tag molecules so that they may be followed through the body of animals. For example, a fat which contains a higher ratio of deuterium to hydrogen one than the ordinary ratio of 1:6000, is used by the cells of an animal in the same manner and at the same rate as ordinary fat. The chemist can, however, separate the fat from the tissues of the animal carcass, analyze these fats by oxidizing them to carbon dioxide and water, and discover what has become of the tagged fat. The water produced on analysis from the fat which contains a high ratio of deuterium, will have a higher density than ordinary water. By use of this technique a great deal has been learned of the fate of fats after they are absorbed in the bodies of animals. This technique has been applied and is being applied to other biochemical problems.

Radioactive isotopes are even easier to trace through the body, since they continue to give off radioactive emanations which can be detected with a Geiger counter or similar device. Radioactive isotopes of the lighter elements which do not occur naturally are being prepared in the atomic piles. Radioactive carbon, for example, is being prepared in fairly large amounts for biochemical research. Compounds can be synthesized which contain this radioactive element, and when they are fed to animals they can be traced through the body.

NEW TERMS

Nucleus, alpha rays or particles, beta rays or particles, gamma rays, proton, neutron, valence electron, isotope, electrovalence, covalence, coordinate covalence, shared electrons, radioactivity, radioactive series, half-life period, nuclear reaction, artificial radioactivity, fission.

QUESTIONS

1. What is the atomic number of an element? The atomic weight?
2. Explain why many atomic weights are not whole numbers. Take a specific element and show how your answer applies to it.
3. What is the relative size of the nucleus and the atom?
4. What are the basic particles of which atoms are composed? What are the characteristics of these particles?
5. What is electrovalence? Covalence? Which elements tend to be electrovalent and which covalent?
6. Which elements are inert? How does the atomic theory explain their lack of reactivity?
7. Draw diagrams of the elements from atomic number 11 through 18. What valence can you predict for these elements?
8. Which of the following compounds will be electrovalent and which covalent? CaCl_2 , PH_3 , CH_3Cl , NaBr , SiF_4 ?
9. Diagram the structure of the atoms in the molecules CH_4 , Li_2O , MgS , CO_2 , NH_3 .
10. Why does the isotope of hydrogen, hydrogen 2, have the special name deuterium? How has deuterium been used as a research tool in nutrition and biochemistry? Is deuterium different chemically from hydrogen 1?
11. What is meant by the term "radioactive"? What is a nuclear reaction? How does it differ from a chemical reaction? A physical reaction?

12. Which elements are radioactive in nature?
13. What is the nature of the alpha, beta, and gamma rays? What is "artificial radioactivity"? How has it been accomplished?
14. Show the nuclear reaction in the following changes by diagramming the nucleus. Name the products.
 - a. Radon, atomic number 86, atomic weight 222, emits an alpha particle.
 - b. Lead, atomic number 82, atomic weight 214, emits a beta particle.
 - c. Thorium, atomic number 90, atomic weight 232, emits an alpha particle.
15. Radon has a half-life period of 3.825 days. What does this mean?

Acids, Bases, and Salts

In Chapter 5, an acid and a base were briefly described. You will remember that an acid is a substance which has a sour taste, changes indicators, and neutralizes bases — it produces hydrogen ions. Bases are substances which have a bitter taste and slippery feeling, change indicators, and neutralize acids. Bases produce hydroxide ions (OH^-), which are negative. Now, some of the reactions of these substances and of that other large group of inorganic compounds, the salts, will be studied. Salts are compounds which have a positive ion, not hydrogen, and a negative ion, not hydroxide.

ACIDS

Their Names

You have already encountered a number of acids, and in the laboratory you have no doubt become familiar with four or five. You probably know sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, and acetic acid, and their names no longer sound strange to you. The general method of naming acids is the following:

1. Ternary acids (acids containing hydrogen, oxygen, and another element).
 - a. Most common acid. Use root of name for distinguishing element and add “-ic.” *Examples:* sulfuric, H_2SO_4 ; phosphoric, H_3PO_4 ; chloric, HClO_3 ; nitric, HNO_3 ; carbonic, H_2CO_3 ; arsenic, H_3AsO_4 .
 - b. Acids containing one less oxygen atom than the “-ic” acid. Use root of name for distinguishing element and add “-ous.” *Examples:* sulfurous, H_2SO_3 ; phosphorous, H_3PO_3 ; chlorous, HClO_2 ; nitrous, HNO_2 ; no “carbonous”; arsenious, H_3AsO_3 .

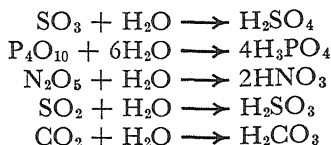
- c. "Hypo—ous" acids contain two less oxygens than the "—ic" acids: hypochlorous, HClO .
- d. "Per—ic" acids contain one more oxygen than the "—ic" acids: perchloric, HClO_4 .
2. Binary acids (acids containing hydrogen and another element). Root of distinguishing element is preceded by "hydro—," followed by "—ic." *Examples:* hydrochloric, HCl ; hydroiodic, HI ; hydrosulfuric, H_2S ; hydrobromic, HBr .

Preparation of Acids

There are two *general* methods for the preparation of acids and a number of special methods.

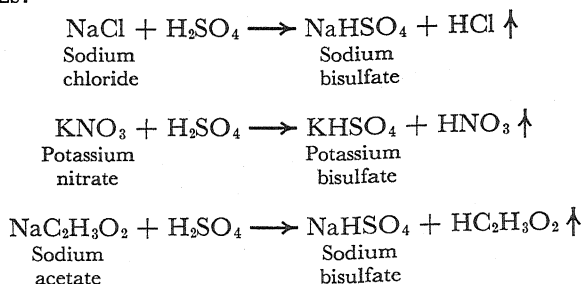
1. Reaction of an oxide + H_2O to produce a ternary acid.

EXAMPLES:



2. Salt + H_2SO_4 to produce a volatile acid. Sulfuric acid has a high boiling point. If a mixture of the salt of a volatile acid and sulfuric acid are heated, the volatile acid is driven off from the reaction medium.

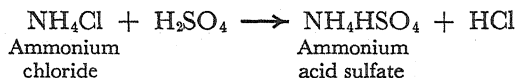
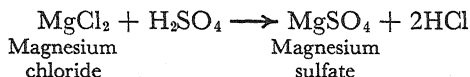
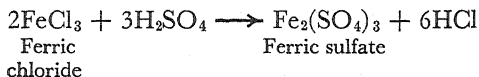
EXAMPLES:



The nature of the positive ion of the salt is not important, if the salt is soluble enough to react. Thus for the preparation of hydrochloric acid, any chloride except silver, mercuric, and lead

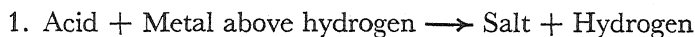
which are not very soluble, can be used. The general reaction indicates the course of the specific reactions.

EXAMPLES:

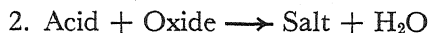
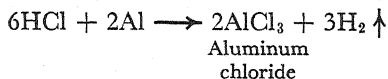
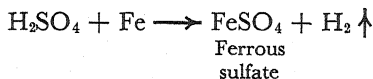


Reactions of Acids

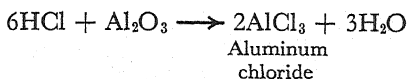
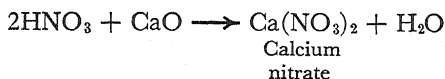
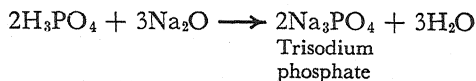
Acids show the following general reactions. If you know the general reaction, you can then predict what any particular reaction will be and can write the equation for it.



EXAMPLES:

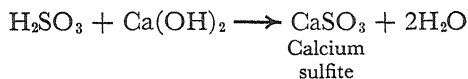
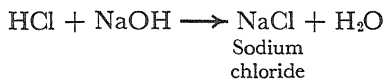
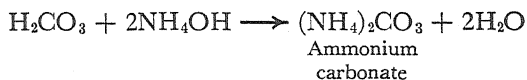


EXAMPLES:



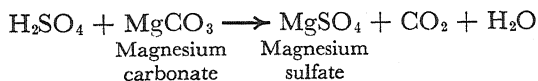
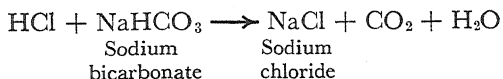
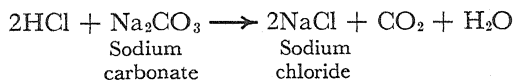
3. Acid + Base \longrightarrow Salt + H_2O . This type of reaction is called *neutralization*. The properties of both the acid and the base disappear as the reaction occurs.

EXAMPLES:



4. Acid + Carbonate or Bicarbonate \longrightarrow Salt + CO_2 + H_2O

EXAMPLES:



Acids which contain *one* potential hydrogen ion are called "*monobasic*." They are acids which will neutralize bases containing one hydroxide ion in the ratio of one molecule to one molecule. Acids containing *two* potential hydrogen ions are called "*dibasic*," and those with *three* potential hydrogen ions are "*tribasic*."

EXAMPLES:

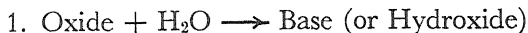
<i>Monobasic</i>	<i>Dibasic</i>	<i>Tribasic</i>
HCl hydrochloric	H_2SO_4 sulfuric	H_3PO_4 phosphoric
HNO_3 nitric	H_2CO_3 carbonic	H_3PO_3 phosphorous
HNO_2 nitrous	H_2S hydrosulfuric	H_3AsO_4 arsenic

BASES

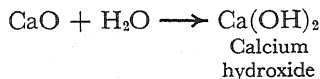
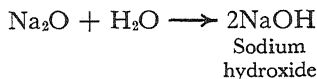
Hydroxides are named by giving the name of the positive ion and then adding hydroxide.

Preparation

In general, soluble bases can be prepared by the reaction of an oxide with water.



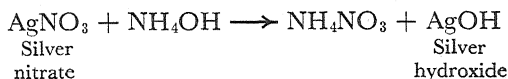
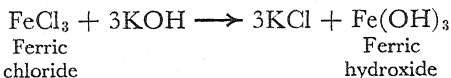
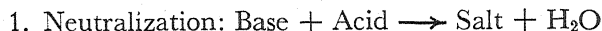
EXAMPLES:



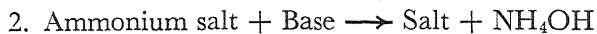
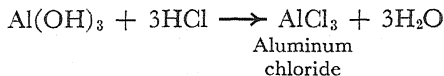
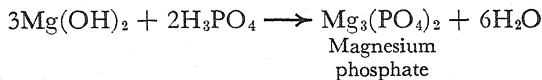
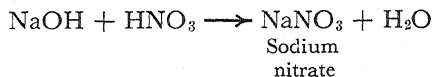
Insoluble hydroxides cannot be prepared by this method, but must be synthesized from soluble salts and a soluble hydroxide.



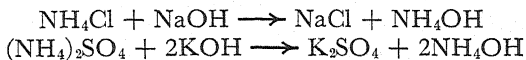
EXAMPLES:

**Reactions of Bases**

EXAMPLES:



EXAMPLES:



SALTS

Salts have been defined on the basis of the ions which make up the molecule, i.e., a positive ion which is not hydrogen and a negative ion which is not hydroxide. From this definition, it can be seen that the number of salts possible is very large. You can undoubtedly write the formulas for a number by using the positive ions which you know with the various negative ions. Thus, there are sodium chloride, NaCl , sodium nitrate, NaNO_3 , sodium sulfate, Na_2SO_4 , sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$, sodium phosphate, Na_3PO_4 , and many others.

Names of Salts

Salts are named by giving the name of the positive ion and the name of the negative ion. The negative ions are named in the following manner:

1. If the negative ion is composed of only one element, the root of the name of that element is used plus “-ide.”

EXAMPLES:

Cl^- Chloride O^{2-} Oxide S^{2-} Sulfide

2. If the negative ion is the same as that occurring in an acid ending in “-ic,” the same root is used with the ending “-ate.”

EXAMPLES:

H_2SO_4 Sulfuric acid SO_4^{2-} Sulfate
 H_3PO_4 Phosphoric acid PO_4^{3-} Phosphate

3. If the negative ion is the same as that occurring in an acid whose name ends in “-ous,” the same root is used plus “-ite.”

EXAMPLES:

HNO_2 Nitrous acid NO_2^- Nitrite
 H_2SO_3 Sulfurous acid SO_3^{2-} Sulfite

Normal, Acid, or Basic Salts

Normal salts are salts which contain no hydrogen ion and no hydroxide ion. In other words, all the positive ions are ions other than hydrogen and all the negative ions are ions other than hydroxide. All the sodium salts named in the first paragraph are *normal* salts.

A number of salts of dibasic and tribasic acids occur which contain hydrogen ions as well as other positive ions. These

are *acid salts*. Examples are NaHCO_3 , KHSO_4 , NH_4HS , MgHPO_4 , NaH_2PO_4 . In all these salts you will notice that only part of the hydrogen ion of the original acid has been neutralized. Acid salts of monobasic acids are not possible. These salts are named by one of three methods: —

1. Name all positive ions and the negative ion.

EXAMPLES:

NaHCO_3 Sodium hydrogen carbonate

NaKHPO_4 Sodium potassium hydrogen phosphate

2. For acid salts of dibasic acids, name positive ion other than hydrogen, then say "bi-" for hydrogen and give the negative ion.

EXAMPLES:

NaHCO_3 Sodium bicarbonate

KHSO_4 Potassium bisulfate

3. Precede the name of the positive ion other than hydrogen with a term indicating the *number* of positive ions. One is "mono-," two "di-," three "tri-."

EXAMPLES:

Na_2HPO_3 Disodium phosphite

KH_2PO_4 Monopotassium phosphate

(The terms "primary," "secondary," and "tertiary" are used in the same way. NaH_2PO_4 , primary sodium phosphate.)

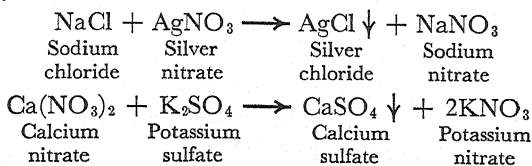
Basic salts occur, but are fairly rare. Basic mercuric chloride, $\text{Hg}(\text{OH})\text{Cl}$, is an example. They are salts produced when a di-acidic base is only partially neutralized.

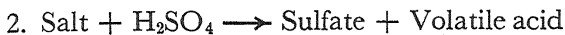
Reactions

Salts will react with one another if one of the products is an insoluble salt.

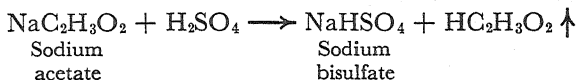
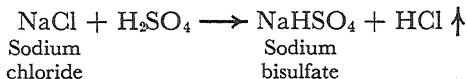
1. Salt + Salt \longrightarrow Salt + Salt

EXAMPLES:





EXAMPLES:



NEW TERMS

Neutralization, monobasic acid, dibasic acid, acid salt, normal salt, basic salt.

QUESTIONS

1. Give the formulas for nitric acid and nitrous acid, sulfuric acid and sulfurous acid. Explain why they have these names. What are names of the salts of these acids?
2. Give a balanced equation for one method by which each of the following may be prepared: nitric acid, acetic acid, sulfuric acid, sodium hydroxide, ammonium hydroxide, sodium sulfate, silver chloride.
3. Give two examples for the preparation of acids from oxides.
4. Give two examples of the preparation of bases from oxides.
5. Give two examples of the reaction of an acid and a base. Why is this type of reaction called a "neutralization"?
6. Name the three sodium salts of phosphoric acid, NaH_2PO_4 , Na_2HPO_4 , and Na_3PO_4 . Name KHCO_3 and K_2CO_3 ; NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$.
7. The following salts are difficultly soluble in water. Give the equation for one method of preparing each salt. BaSO_4 , CaCO_3 , AgBr , Fe_2S_3 , CuS , $\text{Zn}_3(\text{PO}_4)_2$.
8. Complete and balance the following equations:

$\text{NaC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{SO}_4$	$\text{MgO} + \text{H}_2\text{O}$
$\text{HCl} + \text{Al}(\text{OH})_3$	$\text{H}_2\text{SO}_3 + \text{NH}_4\text{OH}$
$\text{HNO}_3 + \text{K}_2\text{O}$	$\text{Ca}(\text{HCO}_3)_2 + \text{HCl}$
$(\text{NH}_4)_2\text{S} + \text{NaOH}$	$\text{Pb}(\text{NO}_3)_2 + \text{KI}$
$\text{Hg}(\text{NO}_2)_2 + \text{NaCl}$	$\text{CuSO}_4 + \text{KOH}$
9. Why do carbonates react with acids to form carbon dioxide?

The Periodic Table

When Dalton announced his atomic theory (see p. 106) in 1808, the progress in chemistry was speeded up since it gave chemists a better understanding of the chemical observations they were making in their laboratories. New elements were continually discovered, and the study of their reactions went forward vigorously. By 1825 a large body of knowledge of inorganic compounds and their reactions had accumulated and although

the Atomic Theory made it understandable, it was not organized knowledge. It soon became apparent that some of the elements were closely related; their reactions and their compounds were not identical, but they were very similar. In 1829 Dobreiner pointed out that there were a number of groups of "triads," three elements with



Fig. 10-1. Mendeleeff
(Courtesy of Journal of
Chemical Education.)

similar properties, and that the atomic weight of the middle member of the triad was approximately the average of the atomic weights of the lightest and heaviest elements. (Some triads which he pointed out were: lithium, sodium, potassium; chlorine, bromine, iodine; calcium, strontium, barium; sulfur, selenium, tellurium.) A number of chemists contributed to the attempts to organize chemical knowledge during the following forty years. Finally in 1869, Mendeleeff, a Russian chemist, published the Periodic Law and in Germany Lothar Meyer added much data to substantiate it. (These two men, working independently, arrived at the same conclusion — the Periodic Law — at approximately the same time. This frequently happens in science, when the time is ripe for some discovery.) The Periodic Law led to the development of the Periodic Table.

In the Periodic Law Mendeleeff stated that the physical and chemical properties of the elements are periodic functions of their atomic weights. Today the Periodic Law states that *the physical and chemical properties of the elements are periodic functions of their atomic numbers*. ("Periodic" here means the same that it does for any function which occurs again and again with some regularity. We find the rising and setting of the sun, the turn of the seasons, our wakefulness and sleep as more or less periodic functions.) When Mendeleeff arranged the then known elements in order of their atomic weights he found that certain physical and chemical properties reoccurred in every eighth or eighteenth element. For example when the formulas for the oxides of the first elements are written, it is found that the type formula reoccurs.

H_2O						
Li_2O	BeO	B_2O_3	CO_2	N_2O_5	—	F_2O_7
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7

Or in the formulas for the hydrides, the same *periodic reoccurrence* may be observed:

LiH	$(\text{BeH})^*$	BH_3	CH_4	NH_3	H_2O	HF
NaH	$(\text{MgH})^*$	AlH_3	SiH_4	PH_3	H_2S	HCl
KH	CaH_2					

* Unusual "Odd molecules."

Lothar Meyer observed the same periodic reoccurrence in such physical properties as the atomic volume (the volume of one gram atomic weight of an element). A modern graph which contains elements not known to Meyer is given which shows that this is true. Sodium, potassium, rubidium, and cesium form the

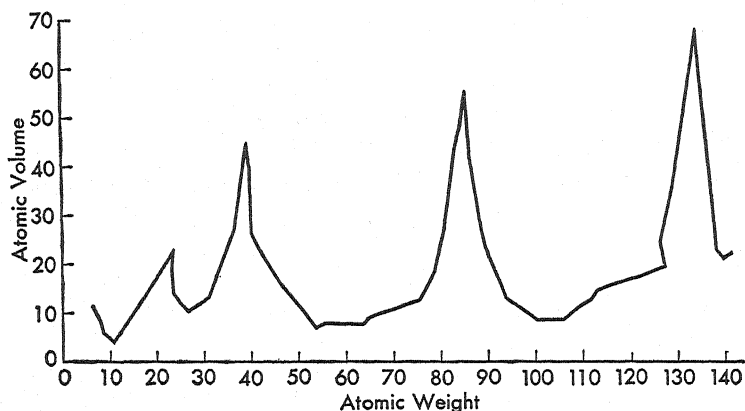


Fig. 10-2. Atomic volume plotted against atomic weight. (Sisler, Van der Werf, Davidson, *General Chemistry—A Systematic Approach*. Copyright, 1949 by The Macmillan Company and used with their permission.)

peaks on the curve. They are not identical elements because the points are not at the same height, but they are certainly similar.

The discovery of the Periodic Law and the formulation of the periodic table had a tremendous impetus on the further development of inorganic chemistry. Mendeleeff was sufficiently convinced that the Periodic Law was universal truth, so that when he found elements apparently out of order, he rearranged them and told the chemical world that there had been errors in measuring the atomic weights of these elements. When the interval between the elements was not eight or eighteen, he was convinced that some elements had not yet been discovered and he left blank spaces for them in the table. His confidence in the law was so great that he predicted in detail the properties of these unknown elements. And he was right.

Here is an example of the surprising accuracy of one of his predictions. (It is one of the best.)

Element 32 — Germanium

	<i>Predicted</i>	<i>Actual</i>
Atomic volume (Vol. of 1 GAW)	72.0	72.3
Specific gravity	5.5	5.469
Boiling point of chloride	100°	86°
Specific gravity of chloride	1.9	1.887
Boiling point of ethyl compound	160°	160°

As knowledge accumulated, the Periodic Table was made more nearly complete. When Moseley started to measure the atomic number of the elements, it became apparent that this is a more reliable method for arranging the elements than the atomic weight. The atomic number of all the atoms of an element are the same, although there is some difference in the atomic weight of different isotopes. Thus all atoms of chlorine have an atomic number of 17, but some have an atomic weight of 35 and some have an atomic weight of 37. Mendeleeff predicted that when the atomic weights were accurately determined, it would be found that the elements fell into the order in which he placed them. This is true in all except three cases: argon, 39.94, precedes potassium, 39.10; tellurium, 127.6, precedes iodine, 126.92; and cobalt, 58.94, precedes nickel, 58.69. When the atomic numbers are used for the classification, there is no irregularity. Argon is atomic number 18 while potassium is 19; tellurium is 52 while iodine is 53; cobalt is 27 while nickel is 28. Today the Periodic Table is arranged with the elements in order of their atomic numbers, rather than their atomic weights.

The modern Periodic Law states that *the chemical and physical properties of the elements are periodic functions of their atomic numbers.*

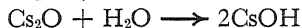
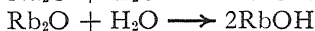
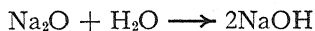
There are several modern arrangements of the Periodic Table, but all are similar except in details. Across the table there are *periods*, each consisting of elements which show a steplike change in their chemical and physical properties as well as a steplike change in their atomic numbers. Thus Period II contains the elements with an atomic number of 3 through 10 while Period IV contains the 18 elements from atomic number 19 through 36.

The elements are arranged in vertical columns called *groups*. All groups except group 0 are composed of two *families*, family A and family B. The arrangement of the elements in families is of great importance since it is the members of these families

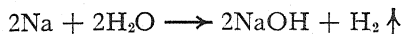
Fig. 10-3. Periodic Table.

which are closely related in their chemical and physical properties. In each group the elements placed at the left of the column are members of family A, while those at the right are family B. In group I lithium, sodium, potassium, cesium, and rubidium form family A while copper, silver, and gold form family B. All members of the group have some properties in common. In group I all are metals, but the resemblances between members of a family are much closer than to other families.

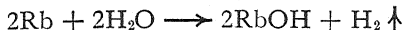
"Family resemblances" will be of great aid to you in remembering chemical knowledge. For example, you are well aware of the fact that sodium chloride is NaCl, while potassium chloride is KCl. Rubidium and cesium, two members of family 1A of which you have probably never heard, will likewise have compounds similar to sodium and potassium. Rubidium chloride will be RbCl and cesium chloride, CsCl. Likewise, the reactions of these compounds will be similar. You are familiar with the reaction of sodium oxide and water to produce sodium hydroxide. Rubidium oxide and cesium oxide will react in similar fashion.



Not only are the compounds of the elements similar, but also the elements themselves show chemical properties which are very similar. You know that sodium is a soft metal which reacts rapidly with water to produce sodium hydroxide and hydrogen.



Rubidium and cesium will show similar properties and reactions. They too are metals.



The members of family 1B, on the other hand, will not show too great resemblances to family 1A although many of their properties will be similar. Family A and family B have a relationship to each other similar to cousins, while members of family A are more like brothers and sisters. Family 1B does show a valence of one and compounds similar to sodium chloride and potassium chloride. There is, for example, cuprous chloride where copper has a valence of one, Cu_2Cl_2 , and you are familiar

with silver chloride, AgCl . This family also shows some variation in valence so that CuCl_2 , cupric chloride, and AuCl_3 , gold chloride, are common compounds. Physically the members of family 1B are also more similar to one another than they are to members of family 1A. Copper, gold, and silver are all metals with high luster, which are hard, and can be drawn out into wires (ductility), or hammered into new shapes (malleability). On the other hand, sodium, potassium, and lithium are soft lustrous metals which soon break if you try to make them into wire or to hammer them into sheets.

In general, family relationships coordinate knowledge and if the chemical reactions of one member of the family are known a great deal is also known about other members of the family. You will remember that the valence of members of family 1 tends to be plus one because there is one electron in the outer shell of the orbits. You will remember that family 2 tends to have a plus two valence. Family 3 tends to have a plus three. Family 4 on the other hand, with four electrons in the outside orbit, tends to form covalent compounds. Family 5, with five electrons in the outer orbit shows various types of compounds. There are compounds in which the element is covalent and some in which the element is plus five, and there are compounds in which the element is minus three. Family 6, with six electrons in the outer orbit, forms compounds in which the element is predominantly minus two. Group 7 with seven electrons in the outside orbit is predominantly minus one, while family 8, the rare gases, with eight electrons in the outer orbit does not form compounds.

There is a gradual change in properties as the atomic weight within a family increases. The change is not as marked as the alteration in members of a period, where there is a conspicuous variation from one member of the period to the next. Chemically the metallic properties of a family increase with increasing atomic weight. Thus every member of family 1A is an active metal with a valence of one when it combines, but cesium, with the highest atomic weight in the family, is the most active metal. Physical properties show a stepwise change with the boiling point and density increasing with increasing atomic weight. The halogens in group 7 are a fine example. The boiling points of the elements are: fluorine, -187°C. ; chlorine, -35°C. ; bromine, 59°C. ; and iodine, 184°C.

We see then that the Periodic Table can be of great value to students since it classifies knowledge. It makes it possible to study families and groups of elements instead of individuals. During the last of the nineteenth century, it was of inestimable help to chemists. It allowed them to predict the properties of unknown elements, stimulated the search for new elements, and led to more accurate determinations of atomic weights.

There are some irregularities in the table which represent disadvantages.

1. The relationship between the characteristic chemical and physical properties of the elements are qualitative and not quantitative relationships.

2. There is no real place for hydrogen; although it has a valence of one and is put, therefore, in family 1, it does not closely resemble these alkali metals. It does not exist as a metal. Its compounds such as HCl, hydrogen chloride, are not very similar to the compounds of sodium and potassium, NaCl and KCl.

3. There is no place for the Transition Elements. These are the elements which are commonly placed at the right of the table and which come between a member of family 7A and family 1B. Examples of this are iron, cobalt, and nickel.

4. There is no real place for the Rare Earths. The Rare Earths are a group of elements which are very similar chemically and physically and which constitute the elements between atomic number 57 and atomic number 71. Instead of observing a stepwise change in characteristics, we find similar characteristics in this group of elements. All of them belong in family 3A. It is therefore impossible to produce a Periodic Table which has a place for these elements without making a kind of appendage to it.

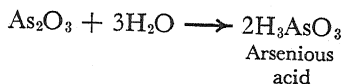
5. There are some elements which have marked similarities but which are separated in the Periodic Table. An example of this is barium and lead. Despite these irregularities you will find the Periodic Table of great interest and importance to you.

Metals and Nonmetals

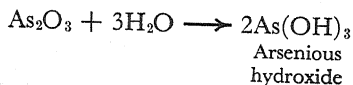
The elements which have properties commonly associated with metals, luster, ductility, and malleability, and some degree of hardness, and which form compounds where they are the positive ion, are called *metals*. These elements occur on the left-hand side

of the table — in other words, family 1, 2, or 3. Across the bottom of the table, the heavy elements are metals. The nonmetals are elements which do not have the physical properties of metals, and likewise which form compounds in which they occupy the negative ion. These elements are in the families A in the upper right-hand corner of the table. Between these metals and nonmetals is a group of elements which are called *amphoteric*.

An *amphoteric element* is one which has properties of both a metal and a nonmetal. Sometimes the properties of the nonmetal predominate, sometimes the properties of the metal predominate. For example, arsenic, element 33, forms arsenious oxide, As_2O_3 . This oxide will react with water to form an acid, a property characteristic of nonmetals.



But it also reacts with water to form a hydroxide, a property characteristic of metals.



Arsenic happens to show a greater tendency to act as a nonmetal and to form an acid than it does to act as a metal and form a hydroxide. (In the presence of a base such as sodium hydroxide, As_2O_3 will react to form an acid. In the presence of an acid as HCl , As_2O_3 will react to form the hydroxide.)

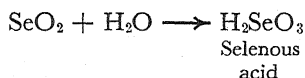
The tendency of an element to act as a metal increases with its atomic weight. Thus the element bismuth, number 83, from the same family as arsenic, family 5A, shows many properties common to metals, few that are common to nonmetals. Both arsenic and bismuth would be classified as amphoteric elements since both of them show some properties of metals and some properties of nonmetals.

If you know which elements are metals and which elements are nonmetals, you then also know which oxides will react with water to form acids and which oxides will react with water to form hydroxides. You will not be able to predict which ones will be nonreactive with water. You can predict that element 48,

cadmium, will form an oxide, CdO , since it is in the family 2B. Likewise you can predict that this oxide will react with water to form a hydroxide.



You know that sulfur, element 16, forms an oxide, SO_2 , which reacts with water to form sulfurous acid, H_2SO_3 . You can therefore predict that selenium, element 34, will form an oxide, SeO_2 , and that this oxide will react with water to form an acid.



Try to get in the habit of using the Periodic Table not only to help your memory, but also to suggest facts to you. You will find that as your use and understanding of the Table increases, so does the aid which it can give you.

NEW TERMS

Periodic law, periods, families, amphoteric element.

QUESTIONS

1. Pick out the elements which are members of family 2A, 2B, 7B.
2. What elements have properties which are similar to phosphorus? To sulfur? Write the formula for phosphoric acid and then write the formulas for the "-ic" acids of arsenic and antimony. Write the formulas for the sodium salts of these acids.
3. Silicon forms a compound with hydrogen just as carbon does. What is its formula?
4. You know zinc and its compounds. Predict what the formulas for the following compounds of cadmium (element 48) will be: sulfide, chloride, hydroxide, nitrate.
5. Why was the Periodic Table useful in the discovery of new elements? Francium is a new element which is produced in the decay of neptunium. It has an atomic number of 87. What element would you expect it to resemble?
6. What are the disadvantages of the Periodic Table? What are the advantages?
7. Where do the metals stand in the Periodic Table? The nonmetals?
8. Why are the Rare Earths usually placed at the bottom of the table?

Water and Its Uses

Water is the most abundant compound which is encountered in our daily life. Your body is composed of 65 per cent water and if you dried up, there would not be much to "blow away." The ocean covers about three-quarters of the earth's surface and even the "dry land" has a portion of water in it, indispensable to the vegetation on it. Almost all foods contain water. Corn flakes are 4.3 per cent water and some foods, like lettuce and cucumbers, are as much as 95 per cent.

THE CHEMISTRY OF WATER

Composition

From ancient times down through alchemical days, water was considered one of the elements. It, along with fire, air, and earth, was believed to be one of the basic ingredients out of which everything was made. In 1788 Cavendish first synthesized water by exploding a mixture of hydrogen and oxygen. These elements were being carefully studied in several laboratories at that time, but Cavendish's knowledge of them was not complete enough for him to realize fully the significance of his observations. Lavoisier, at the same period, observed that water was decomposed when steam is passed over hot iron to form hydrogen.

Later these experiments were repeated many times, and eventually it became apparent that this material, water, could be synthesized or decomposed and that it was, therefore, not an element but a compound.

The exact composition of water was very carefully investigated by E. W. Morley during the last few decades of the nineteenth century. By that time delicate analytical balances had been developed and it was possible to make accurate observations.

He carefully weighed hydrogen and oxygen, allowed them to react, removed and weighed the unreacted gas, and calculated the ratio by which they react. After many duplicate determinations, he concluded that 2.016 parts of hydrogen by weight reacts with 16 parts of oxygen, or 1 part of oxygen by volume reacts with 2.0024 parts of hydrogen. This gives the formula H_2O when it is calculated according to the method given in Chapter 4.

$$\begin{aligned} 2.016 \text{ g. hydrogen} \div 1.008 \text{ (at. wt. H)} &= 2 \text{ atoms} \\ 16.000 \text{ g. oxygen} \div 16 \text{ (at. wt. O)} &= 1 \text{ atom} \\ \text{Empirical formula} &= H_2O \end{aligned}$$

The composition of water can also be demonstrated by analysis. A crude analysis can be carried out by electrolyzing water and measuring the amount of hydrogen and oxygen produced. Twice the volume of hydrogen is obtained as of oxygen. This indicates that there are twice the number of hydrogen atoms in water as there are oxygen. This method does not give accurate results, however, because some of the oxygen is evolved as ozone, O_3 , instead of O_2 .

Determination of the molecular weight of water shows it to be approximately 18. This means that the molecular formula must be H_2O .

Natural Waters

You are well acquainted with the water cycle in nature since it is a part of your daily life. Water falls as rain, it soaks down through the soil or runs off in streams and rivers to the ocean. Part is evaporated and falls again as rain. Part is consumed by animals and is excreted in sweat, expired air, urine, and feces. Plants absorb large quantities of water and evaporate it from the leaves (transpiration).

No natural water is absolutely pure water. It must be carefully processed before the impurities may be removed. Some of us think of rain water as very pure water, but actually there are many substances dissolved in it. Rain water as it falls to earth dissolves air, picks up dust particles, both organic and inorganic, and other materials from the atmosphere. Along the sea coast rain will contain salt, while near large factories it will contain

sulfur compounds from the smoke residues. It may contain pollen grains and small insects.

Surface water will contain material dissolved as the water runs over the soil and a great deal of material which is simply carried along such as sand and clay, bark and decaying leaves, bacteria, molds, and yeasts. Spring water is water which has percolated down through the soil and then come to the surface, usually at a lower level. The organic matter and many microorganisms are removed as the water trickles through sand and soil, but soluble substances in the soil are dissolved. If the amount of salts in spring water is particularly high (or if it has an unusual composition) it is called mineral water.

Water from a well is underground water with a composition similar to spring water. The salt content varies with the nature of the material over which the water has trickled, and it is usually free of harmful microorganisms, if the well is deep and there are no sources of high contamination, such as privies, close by.

Water in the seas and oceans has a relatively high salt content since salts are continually being added with the water from rivers, but only water is removed by evaporation. The salt concentration is about 3.5 per cent, although the Dead Sea and Great Salt Lake have a higher concentration.

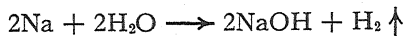
Composition of Sea Water

<i>Positive Ions</i>		<i>Negative Ions</i>	
Sodium	1.06%	Chloride	1.90%
Magnesium	0.13	Sulfate	0.26
Calcium	0.04	Bromide	0.006
Potassium	0.038		

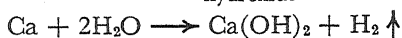
Chemical Reactions

Water reacts chemically with several different types of compounds as well as acting catalytically in a greater number of reactions.

1. Metals + Water \longrightarrow Hydrogen + Oxide or Hydroxide. The metals at the top of the Electromotive Series Chart, you will remember, are the most active chemically. They will react with cold water. When sodium is dropped in water it reacts violently.



Sodium
hydroxide

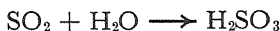


Calcium
hydroxide

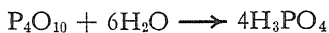
Those metals which stand close to hydrogen in the Electromotive Series react slowly with steam, while those below hydrogen do not react with water to replace hydrogen from its compound.

2. Oxides + Water \longrightarrow Acids or Bases. Nonmetallic oxides combine with water to form acids, while metallic oxides form bases. A large number of oxides and hydroxides are insoluble and do not react. Thus:

Nonmetallic oxides

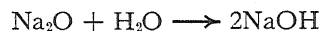


Sulfur
dioxide Sulfurous
acid

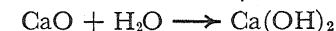


Phosphorous
pentoxide Phosphoric
acid

Metallic oxides



Sodium
oxide Sodium
hydroxide



Calcium
oxide Calcium
hydroxide



Ferric
oxide

Some insoluble oxides are CuO , Ag_2O , Al_2O_3 , SiO_2 , and CrO_3 .

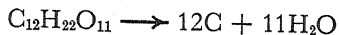
3. Hydrate formation. A number of substances, particularly salts, combine with water to form hydrates. The hydrates are chemical compounds with their own properties and a definite composition, but most of them are unstable. They decompose and lose water readily, but they are also easily synthesized from the anhydride (without water) and water. Thus anhydrous copper sulfate, a grayish white powder, reacts readily with water to form a number of hydrates, the most common, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, which forms large bright blue crystals.



This reaction is very easily reversed. The copper sulfate hydrate decomposes rapidly when it is warmed or even when it is held at

room temperature in a dry atmosphere. *A hydrate is a substance which readily decomposes to form water and is readily resynthesized.*

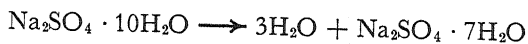
On the basis of this definition carbohydrates are not true hydrates. Many carbohydrates will decompose to form water when they are heated strongly, but the dark sticky residue will not react again with water to form the original compound. Part of the dark residue is carbon which has been formed by the following reaction:



Commonly the formulas for hydrates are written in such a way that the hydrate structure is emphasized. It could be written $\text{CuH}_{10}\text{SO}_6$, but the products of decomposition would not be so evident. The dot in the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ indicates that a chemical bond exists.

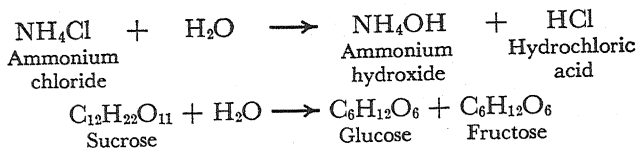
A few other examples of hydrates are $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $2\text{NaOH} \cdot 7\text{H}_2\text{O}$.

All these substances will decompose when exposed to dry air. Those that are crystals will crumble to powders. This loss of moisture to a dry atmosphere by a hydrate is called *efflorescence*. The other product is sometimes a lower hydrate and sometimes the anhydride.



In a moist atmosphere, water will condense on some crystals and form a saturated solution. The crystals become sticky and will eventually go into solution completely. The condensation of water on crystals from a moist atmosphere is called *deliquescence*. You have observed this phenomenon on the salt in a salt shaker in the summer. Calcium chloride is effective in laying dust on a road because of its marked ability to pick up moisture from the air. In the case of common salt, NaCl , the action occurs because the saturated solution of sodium chloride which is formed around every crystal has a lower vapor pressure than moist air. The calcium chloride forms hydrates which augment the effect.

4. Hydrolysis. Water reacts with many compounds to give double decomposition reactions. These are called hydrolysis reactions. There are examples not only in the field of inorganic chemistry but also in organic chemistry.

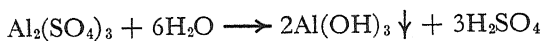


5. Catalysis. Water is perhaps the most common catalyst which is experienced. Many compounds which react in an aqueous medium are completely unreactive when dry. The water is acting as a catalyst. You are familiar with the fact that baking powder will keep indefinitely if it is protected from moisture, but as soon as the fluid of a batter is added, small bubbles of carbon dioxide begin to rise through the mixture. Water catalyzes the reaction. Zinc will not react with dry hydrogen chloride, and many acids will not neutralize bases. In each of these reactions water acts as a catalyst.

WATER IN THE HOME

Drinking Water

Drinking water in the United States is obtained from many sources, wells, rivers, lakes. The prime concern in considering water for drinking is not in its contamination with chemical compounds but with bacteria. Most people do not relish water with a strong flavor, but if it is not actually brackish and if it is relatively low in bacteria count and free of pathogenic bacteria, it may be used. Water containing a high percentage of hydrogen sulfide is used in some communities. Surface water must usually be purified by settling to remove leaves, twigs, sand, and clay. The clay may be extremely finely divided (in a colloidal state) and can only be precipitated by use of a chemical agent. Aluminum or iron salts are added which coagulate the clay particles and which also hydrolyze to form insoluble hydroxides that in precipitating help carry down the clay.



(See chapter on colloids.) The water may then be filtered through sand or drawn off.

Almost all community water systems add chlorine to water. This agent kills bacteria which are present and insures that no

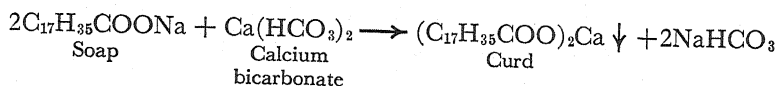
contamination of the water occurs in delivering it to the consumer.

Aeration of water by spraying it through fountains is usually used to improve the flavor of water. Cool boiled water, which contains little air, has a flat taste. Aeration may accomplish the purification of the water by killing the bacteria. In nature streams are purified as they are aerated. A brook, bouncing over rocks, dashing into a spray, may be free of bacteria a short distance from the point of contamination, while a slow, sluggish stream will carry the bacteria for a long distance. However, aeration alone is not used in the United States in water purification plants to remove bacteria from water.

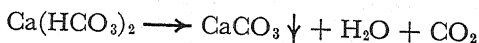
Laundry Water

In considering water for laundering the chemical composition of the contaminants is of great importance. Calcium, magnesium, and iron salts interfere with the action of soap and produce objectionable greasy curds which cling to fabrics, dishes, etc. Underground waters frequently contain these dissolved salts. Water which contains salts that interfere with the detergency of soap is called *hard water*. Water from which the hardness can be removed by boiling is called *temporary hard water*; that from which the hardness cannot be removed by boiling is called *permanent hard water*.

What makes water hard? The calcium, magnesium, or ferric ions which are present when salts of these metals are dissolved as water trickles through the soil react with soap to form insoluble greasy precipitates. The soap can no longer act as a cleaning agent if it has precipitated. Soap is a mixture of the sodium salts (or in a few soaps, the potassium salts) of fatty acids. An example is sodium stearate, $C_{17}H_{35}COONa$, present in most commercial soap. It reacts with calcium, magnesium, or ferric salts according to the following reaction:



Temporary hard water contains the bicarbonates of calcium and magnesium which precipitate as insoluble carbonates on heating.



Permanent hard water contains sulfates and to a limited extent chlorides of calcium, magnesium, and iron. The amount dissolved is in reality quite small. If hardness is measured in terms of parts per million of calcium carbonate, then water has the following approximate characteristics.

<i>Hardness</i>	<i>Quality of water</i>
50 parts per million	Soft
50-100	Moderately soft
100-150	Slightly hard
200-300	Hard
over 300	Very hard

A concentration of 300 parts per million of calcium carbonate (or its equivalent) represents the concentration of a solution of 300 milligrams of calcium carbonate in 1 liter of water.

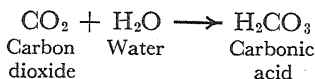
Development of Hardness

The most common type of hard water is the temporary hard water drawn from wells and occasionally springs in limestone areas. In these widespread areas, a cap of limestone, primarily calcium carbonate, CaCO_3 , lies under the subsoil, and rain water trickling down through the soil passes through cracks in it. The rain water is not pure water, but a very dilute solution of the gases of the atmosphere. Some carbon

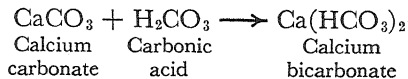


Fig. 11-1. Boiler scale deposited in a section of hot water pipe. The scale is calcium carbonate with some brown ferric carbonate. Limed pipes are an expense since they must be replaced.

dioxide is dissolved, yielding a very dilute solution of carbonic acid.



The carbonic acid reacts with the relatively insoluble carbonates to form soluble bicarbonates.



Slowly the rock is dissolved away. The effect can be seen in the limestone tombstones erected a hundred or a hundred and fifty years ago. The letters cut in the stone are often almost worn away by this reaction and by the abrasive effect of wind-blown sand and dust.

Permanent hard water is produced by simple solubility. Calcium sulfate, magnesium sulfate, ferric chloride, and ferric sulfate are dissolved as water soaks through soil.

Temporary hard water is particularly expensive and objectionable to use in any hot water system. Boilers, pipes, and kettles become coated and finally clogged with "boiler scale," the precipitated carbonates. The scale interferes with the flow of water, increasing pressure, as well as with the transfer of heat.

It is in the laundry and kitchen where most housewives find grievances against hard water. The hardness necessi-

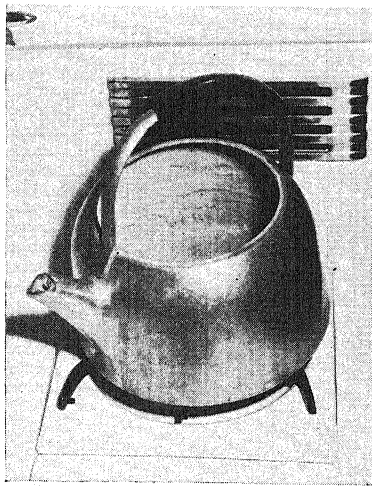


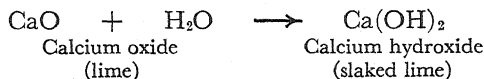
Fig. 11-2. Boiler scale deposited in a tea kettle. Temporary hard water has been heated repeatedly in this kettle and has slowly built up a deposit of calcium carbonate. Small amounts of iron carbonate give a pale brown tint to the deposit.

tates the use of more soap, precipitates a film difficult to remove, and retains dirt particles. The result is gray, streaked laundry. It also appears to make roughness and chapping of skin more frequent than when soft water is used. It presents some cookery problems.

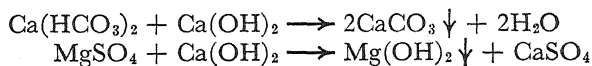
Softening Water

Hard water, either temporary or permanent, may be softened (1) by precipitating the calcium and magnesium ions, (2) by substituting sodium ion for the calcium or magnesium, or (3) by tying up the calcium ion in a nonionized complex (sequestering).

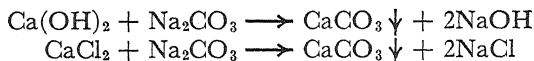
1. A number of precipitating agents may be used. (a) *Soda-lime*. In large-scale softening of water for a community or a large industry soda-lime affords a cheap and practical method of reducing the hardness in water to about 50 parts per million. Soda is sodium carbonate and lime is calcium oxide, CaO , or "slaked lime" Ca(OH)_2 may be used.



First, lime is added to the water in large settling tanks. Here it reacts to form calcium hydroxide. This base then reacts with calcium bicarbonate to form the far less soluble carbonate while magnesium ions are precipitated as the hydroxide.



The excess Ca(OH)_2 , as well as other calcium salts, is precipitated by the subsequent addition of Na_2CO_3 .



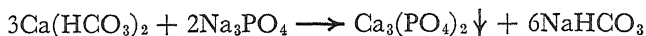
The water is settled, and the clear soft water runs off. The water now contains sodium salts in place of calcium salts, but these do not react with soap.

(b) Washing soda, Na_2CO_3 , is commonly used as a water softener in the home. It precipitates the calcium ion effectively but not the magnesium. However, the water may be very

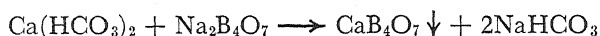
appreciably softened since in all hard waters, it is the calcium ion which is the chief offender.



(c) TSP, trisodium phosphate, Na_3PO_4 , is present in many of the mixed water softeners. It is available at many hardware and paint stores, but, in the experience of the author, it is not used frequently as the pure compound in the home.



(d) Borax, $\text{Na}_2\text{B}_4\text{O}_7$, also precipitates the calcium ion and is fairly widely used by housewives, particularly in laundering and washing painted surfaces.



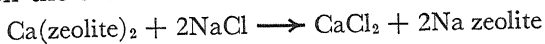
All these water softeners precipitate the calcium ion as an insoluble calcium salt and replace this ion with the sodium ion. The formation of a finely divided white precipitate in a wash water is far from desirable. It leaves a white powder on dishes and glassware, and garments gradually develop a gritty feeling. However, this type of precipitate is far less objectionable than the greasy precipitate of calcium soap. It is also less expensive to use borax, ($\text{Na}_2\text{B}_4\text{O}_7$), TSP (Na_3PO_4), or washing soda (Na_2CO_3) as the precipitating agent than to let soap do the job of removing the calcium ion.

2. The water softener units, used in homes and often in industry, substitute a sodium ion for the calcium or magnesium ion, but do not form a precipitate. They are, therefore, in general, more satisfactory in hard water areas than the use of water softeners in small quantities of water. All these units contain a complex sodium aluminum silicate, called a zeolite, which has the ability to form an equilibrium reaction with calcium salts. These zeolites have various trade names such as Permutit, Re-finite. Some occur in nature, while some are prepared synthetically. As water flows over the zeolite, the ion exchange takes place on the surface and the calcium and magnesium ions are retained.



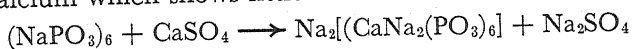
The zeolite eventually becomes loaded with calcium and magnesium ions and is depleted of sodium ions. Its efficiency falls

until finally it is no longer effective. However, the reaction can be reversed and the calcium and magnesium ions can be replaced by sodium ions. The recharging is accomplished by passing a concentrated brine (NaCl solution) over the zeolite and then flushing off the excess salt.



The chief disadvantage of this water softener is the fluctuation of hardness in the water from a low level, just after recharging the zeolite, to a relatively high hardness just before recharging.

3. There is one other type of water softener available — a salt which forms a poorly ionized calcium salt. The product available for home use is Calgon and is a hexa sodium metaphosphate, $(\text{NaPO}_3)_6$. It has the ability to form a complex ion with calcium which shows little dissociation.



The complex salt forms the ion, $\text{CaNa}_2(\text{PO}_3)_6^-$. This salt is soluble and there is, therefore, neither a powdery nor a greasy precipitate formed when soap is added to water which has been treated with Calgon.

The waste of soap which occurs in hard water through the formation of insoluble calcium and magnesium soaps is considerable. It has been calculated that a family of five, using water with a hardness of 400 parts per million, will waste 138 pounds

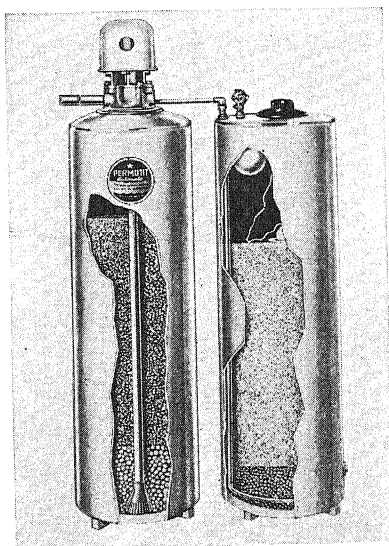


Fig. 11-3. Diagram of an automatic household water softener. The tank on the left contains Permutit, a type of silicate which exchanges sodium ions for calcium ions as the water passes over it. The tank on the right contains coarse salt, NaCl, and a salt solution, used to recharge the Permutit. (Courtesy of the Permutit Company.)

of soap a year in reaction with the calcium and magnesium ions. Soap is an expensive water softener. At the 1950 price of 22 cents per pound this would represent a cost of \$30.36. Perhaps the cost of the soap is the least expensive item in the hard water bill when the damage to fabrics caused by the precipitation of soap is considered. The problem of laundering fabrics is discussed further in Chapter 34.

Hard Water in Cooking

Hard water is not only objectionable in the laundry but also in cooking certain foods. Navy beans and peas do not cook to a soft consistency in very hard water. It has been shown that beans canned with 100, 200, 300, 400, 500, 600, and 1000 parts per million of calcium chloride are progressively harder although cooking and canning procedures are otherwise identical. The reaction is probably one of the calcium ion of the hard water with the pectic acid to form calcium pectate which is insoluble.

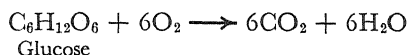
In canning tomatoes, advantage is taken of this reaction to increase the firmness of the fruit. The addition of small amounts of calcium chloride to the pack increases the firmness of the tomato by forming insoluble calcium pectate in the cell walls or interstices.

In preparing tea and coffee, hard water results in a muddy looking extract instead of the sparkling clear beverage considered desirable. This is particularly noticeable in iced tea where precipitation is likely to be more complete and at the lower temperature more extensive. The precipitate is composed of the calcium and magnesium salts of the tannins. In coffee the same reaction takes place to a lesser degree. The reddish brown precipitate forms on the surface of the liquid and clings to the sides of the cup. Completely softened water does not give a precipitate since the sodium tannates are not insoluble. It is, therefore, necessary in hard water areas to use softened water in order to produce a clear extract of coffee or tea.

In Your Body

Water is the principal compound of the body and it is of major importance to the normal functioning of the body. Cells cannot live without water, and all the chemical reactions of the body occur in an aqueous medium. The transportation of

nutrients to the cells and of waste products away from cells is accomplished by the "fluid tissues," blood, lymph, and the intercellular fluid. Water enters into many reactions of the body. For example, all the chemical reactions which comprise digestion are hydrolysis reactions. Water is sometimes a product of the reactions which occur in cells. The overall reaction for the oxidation of glucose is:



Water which is a product of chemical reactions in the body is called *metabolic water*. The presence of water in our excrement is likewise of prime importance. The water in urine holds waste products dissolved in it. The water present in feces makes them soft and easily evacuated. The water in the expired air maintains the tissues over which it passes in a moist and pliable state. The water of sweat cools the body and helps maintain the body temperature within a limited range. Water has many functions — important functions — in the human body.

NEW TERMS

Hydrate, hydrolysis, efflorescence, deliquescence, mineral water, temporary hard water, permanent hard water, softened water.

QUESTIONS

1. What evidence is there that a molecule of water contains two hydrogen atoms and one oxygen atom?
2. Why is it incorrect to call rain water "pure" water?
3. Why does well water usually have salts dissolved in it?
4. Why is well water usually safe for drinking? How might it be contaminated? Is spring water safe for drinking?
5. What elements will react with water to form hydrogen? Give examples by writing balanced equations.
6. Give two examples of the reaction of a metallic oxide with water. Use balanced equations. Give two examples of the reaction of non-metallic oxides.
7. What is a hydrate? Why are carbohydrates not true hydrates?
8. Why is calcium chloride effective in keeping down dust on a road in summer?

9. Why is water called a catalyst for many reactions?
10. Why is some water hard? How does it get hard? Give three methods for softening water in the home.
11. What are the disadvantages of hard water in the home?
12. What salts in hard water interfere with the lathering of soap? Give the equation.
13. Why does lime deposit in the bottom of a tea kettle if hard water is constantly heated in it? Give equation. What is the chemical difference between temporary hard water and permanent hard water?
14. Is hard water objectionable or desirable in cooking? Give examples.

Solutions

Everywhere you turn, every day you live, you come in contact with solutions. Some of your drinks are simple solutions while your solid foods contain solutions mixed in them. You make solutions when you add salt to water, stir sugar in your coffee, remove a grease spot from your dress with carbon tetrachloride. Your own body is composed of many complex and intricate solutions. Food undergoes digestion and then is dissolved before it is absorbed into your bodies. Gasoline, rain water, and air are all solutions.

A solution is a homogeneous mixture of molecules or of molecules and ions. A mixture is called homogeneous because the smallest drop has the same composition and the same properties as the whole solution. If it is examined with a microscope, if samples of different parts of the solution are analyzed, it is always the same. A solution is said to be a mixture of molecules or of molecules and ions because study of the particle size of the components of the mixture reveals that they are exceedingly minute and that they behave like particles the size of ordinary molecules and ions. If the size of some of the molecules is very large, as in protein molecules, the mixture no longer behaves like a solution.

The two components which make up this very special type of mixture, a solution, are the *solute* and the *solvent*. The solvent is usually designated as *the substance present in greater amount*, while the solute is *the substance present in smaller amount*. So when one teaspoon of sugar is added to a cup of water, the sugar is called the solute and the water is the solvent. Occasionally this designation is not followed. When one of the components is commonly encountered as a solvent and in a rare case is present in lesser amount, it may still be called the solvent. Water is the most common solvent in general experience, and when occasionally a solution is used in which there is less than 50 per cent water, still, out of habit, the water is often called the solvent.

It is possible to have nine different types of solutions depending on the state of matter of the solvent and the solute. There are examples of gases, liquids, and solids dissolved in gases; of gases, liquids, and solids dissolved in liquids; and of gases, liquids, and solids dissolved in solids. The criteria for designating any mixture a solution are that it is homogeneous and that it is made up of particles the size of molecules and ions. Air is a homogeneous mixture of gaseous molecules and it is therefore a solution of gases in gas. Since the water vapor in air at room temperature is vaporized from liquid water, the mixture can be considered a solution in which the water has dissolved in the nitrogen. Likewise when naphthalene vaporizes into the air, we can consider this an example of a solid dissolving in a gas. There are many examples of solutions in which the solvent is a liquid. A common solution of a solid is sugar, of a liquid is alcohol, and of a gas is air in water. Many of the metal alloys, such as those in a gold ring, in a nickel coin, or in an aluminum pan, are intimate mixtures of metal molecules and therefore true solutions of solids in solids. You are less likely to encounter examples of gases in solids or of liquids in solids. Some metals have the ability to dissolve gases. Palladium, for example, will dissolve hydrogen. The solution of mercury in some metals results in a solution of a liquid in a solid. The accompanying tabulation will give you examples of all nine types of solutions.

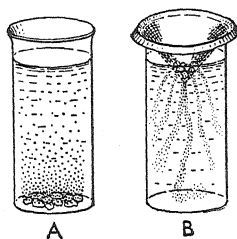
<i>Type</i>	<i>Example</i>
1. Gas in gas	Any mixture of gases such as air
2. Liquid in gas	Water vapor in air
3. Solid in gas	Camphor in air, iodine in air
4. Gas in liquid	Oxygen in water, carbon dioxide in "pop"
5. Liquid in liquid	Water in alcohol, oil in gasoline
6. Solid in liquid	Sugar in water, fat in carbon tetrachloride
7. Gas in solid	Hydrogen in palladium
8. Liquid in solid	Mercury in silver, or silver amalgam
9. Solid in solid	Many alloys, copper in gold

Nature of Solution

What happens when a solution forms? You have seen gases diffuse into one another. You will remember the appearance of brown bromine gas diffusing into air, and you will recall that the gross appearance of the sample suggested that the molecules

were moving about and becoming intimately mixed with one another. You can observe the same effect if you put a colored

Fig. 12-1. The process of solution. The attainment of homogeneity is shown by two simple experiments. In cylinder A large crystals of copper sulfate hydrate are placed in the bottom and water is carefully added. The blue color of the copper ions slowly penetrates the water and eventually the liquid is homogeneous. In cylinder B potassium permanganate is suspended at the top of the cylinder. Dark streamers of purple permanganate ions fall through the water. This arrangement permits a much more rapid attainment of homogeneity.



solid such as copper sulfate at the bottom of a tall thin cylinder and carefully pour water over it so that the solid does not mix with the liquid. Slowly the blue color of the copper sulfate will diffuse up through the water. It may take some months before the mixture is homogeneous, if the cylinder is tall. But every day you will see changes indicating that the solution is becoming more nearly homogeneous. Or you may observe a similar change but in a shorter time if the solid is suspended on a piece of cardboard at the top of the water. You then see streams of color falling through the water to the bottom of the cylinder, turning and rising, until in a short time the mixture becomes homogeneous. Here with heavy solute ions, gravity is helping to mix the solution intimately. An even faster attainment of homogeneity may be produced by stirring the colored solute and the water. In all cases it can be observed that particles too small to delineate with the eye, but apparent in a large mass because of their color, break off from the solid crystals and travel through the solvent. It is concluded that molecules or ions are leaving the solid material and are passing independently between the molecules of the solvent. Eventually as they move about, the mixture will become more homogeneous, and there will be the same number of molecules or ions of the solute in one drop of the solution as there are in any other drop.

Heat of Solution

When a solid dissolves in a liquid or gas, there is a change in energy content. Sometimes when a solute such as sodium hydroxide, NaOH , dissolves in water, a good deal of heat is released.

This is called the positive heat of solution. With other mixtures, quite the reverse occurs. When ammonium chloride, NH_4Cl , dissolves in water, the solution cools. This is called a negative heat of solution. On the basis of the Kinetic Theory, the negative heat of solution is most readily understood. You will recall that the amount of movement of molecules in a solid or of ions in a solid is relatively small. When a solution is formed, these ions or molecules begin to move more freely and must therefore have more energy. Thus when ammonium and chloride ions move off through the solution, they experience considerable increase in motion, and therefore an increase in energy content. That energy can only be gained from the environment. Therefore the temperature of the solution will fall. But what of the sodium hydroxide in water? Surely this too is an example of ions which must gain energy from their environment in order to attain a greater movement. That is exactly true, but besides this, ions of sodium react with the water to form a hydrated sodium ion. This reaction of the sodium ion with water is an exothermic reaction and therefore liberates heat. The positive heat of solution is the result of two forces: (1) the loss of energy due to the increased motion of the ions or molecules and (2) the gain in energy which is due to the exothermic reaction of hydration.

Heat of solution	{	Negative — energy used up by motion of solute
		Positive { energy used up by motion of solute energy produced by reaction with solvent

The extent of solubility will depend on a number of factors.

1. First of all there is the *nature of the solute and the solvent*. Some things show great solubility simply because it is their nature. Others show limited solubility. Thus you are familiar with the great solubility of sugar in water, with the fair solubility of sodium chloride in water, and with the insolubility of glass in water. Sugar, on the other hand, is almost completely insoluble in gasoline or benzene. The extent of solubility depends on the chemical nature of the solvent and the solute.

2. For many substances an increase in *temperature* causes an increase in solubility. This is not always true, however. Some show little effect of temperature on the extent of solubility and some substances, particularly gases, show a decreased solubility

with increased temperature. You have probably all had the experience of opening a warm bottle of pop and having it fizz all over. The solubility of carbon dioxide in warm pop is much less than in cold.

3. The *pressure* on a solution influences the solubility of gases. Increase in pressure increases the solubility of

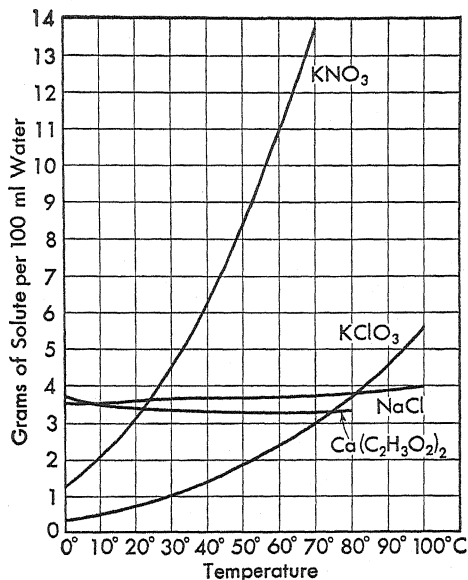


Fig. 12-2. The effect of temperature on solubility.

gases. The solubility of liquids and solids is usually not affected by pressure.

The *concentration* of a solution is a measure of the amount of solute dissolved in a given amount of solvent or of solution. A *concentrated solution* is one which contains a relatively large amount of solute for a given amount of solvent, while a *dilute solution* is one which contains a relatively small amount of solute for a given

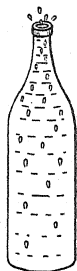


Fig. 12-3. Carbon dioxide gas escapes when the pressure is reduced on soda pop by removing the cap. The solubility of gases in liquids is proportional to the pressure on the solution.

quantity of solvent. A solution may be made more concentrated by adding more solute, or it may be made more concentrated by

evaporating off some of the solvent. The chemical nature of some mixtures which are solutions is such that it is impossible to have a concentrated solution. For example, silver chloride will dissolve in water to the extent of 0.000152 gram per 100 grams of water at 20° C. This would of course be a very dilute solution, and it would be impossible to produce a concentrated solution of silver chloride in water. On evaporating the solution, silver chloride precipitates.

A *saturated solution* is one in which there is an equilibrium between the solution and undissolved solute. If an attempt to increase the concentration of a solution is made by adding more solute to it, ultimately the state is reached where the quantity of solute undissolved remains unchanged. This is the state of *saturation*. Actually some of the undissolved material is dissolving, and some of the solute from the solution is depositing on the crystals of the undissolved material. This is a *dynamic equilibrium*. If a solution is studied which shows an increased solubility with increased temperature and if a saturated solution is produced at the elevated temperature, the mixture on cooling will usually precipitate crystals. For example, a saturated solution of potassium nitrate at 100° C. contains 247 grams of solute. At 0° C. a saturated solution of potassium nitrate in water contains only 13.3 grams per 100 grams of water. In cooling a saturated solution of potassium nitrate from 100° to 0°, 233.7 grams of potassium nitrate will separate from the solution.

Some solutions do not show this phenomenon, but instead produce *supersaturated solutions* as they cool. A sugar in water solution is an outstanding example of supersaturation. If a hot saturated solution of sugar in water is prepared or even a concentrated solution of sugar in water and the solution is then cooled to room temperature or below, there is seldom precipitation of crystals of solute. Instead the solute is held in solution in a supersaturated state. The supersaturated solution is an unstable solution and, very quickly and under numerous conditions, changes state. For example, if a crystal of sugar is added to a supersaturated solution of sugar in water, a great deal of sugar will then crystallize and a saturated solution will be prepared. This is true of all supersaturated solutions. They are readily upset by such factors as stirring, scratching the side of the beaker, dust, and the introduction of crystals. A *supersaturated solution* is

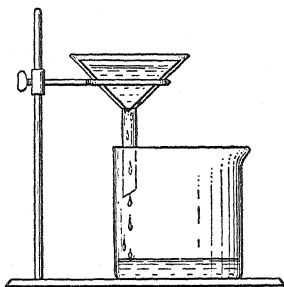
an unstable solution which in contact with undissolved solute precipitates some solute to form a saturated solution. Many other solutions form supersaturated solutions besides sugar and water, but this is the supersaturated solution with which you will probably have most experience in cookery.

Properties of Solutions

Some of the properties of solutions with which you are familiar and some of those which you may not have observed but which will be useful to you will be studied.

1. Solutions do not settle out.
2. Solutions will pass through a filter paper.

Fig. 12-4. A solution passes through a filter paper.



3. Solutions will pass through a dialysis membrane. A dialysis membrane is a membrane with tiny pores which will allow small molecules and ions to pass through but which blocks the movement of large particles such as protein molecules or colloidal aggregates. Some examples are cellophane, parchment paper, the "skin" inside the shell of an egg, the lining of the gastrointestinal tract. Since both the solute and solvent will pass through most dialysis membranes, they may be readily separated in this manner, from larger particles.

4. The vapor pressure of a solution differs from the vapor pressure of the solvent. If at the temperature at which the vapor pressure is measured the solute has an appreciable vapor pressure, then the vapor pressure of the solution will be greater than the vapor pressure of the solvent. For example, a mixture of alcohol and water has a vapor pressure greater than water. Many solutions, however, are composed of a solute which has little or no vapor pressure, and in this case the vapor pressure of the solution is less than the vapor pressure of the solvent. For example, the vapor pressure of salt and water has a vapor

pressure less than the vapor pressure of water at the same temperature. This can be readily demonstrated by a simple experiment. If two beakers, one containing water and one containing a saturated solution of calcium chloride, are placed under a bell jar and observed from day to day, it is discovered that the level of the water in the beaker falls while the level of the liquid in the beaker containing the solution rises. This is readily understood if the Kinetic Theory and the changes that take place when a liquid evaporates are recalled. Over the beaker of pure water there are clouds of water molecules that are made up of those which have jumped off the surface of the water. When the system comes to equilibrium, the number of molecules which leave the surface of the water will be equal to the number of molecules which fall back into the water. The other beaker

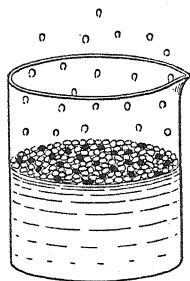


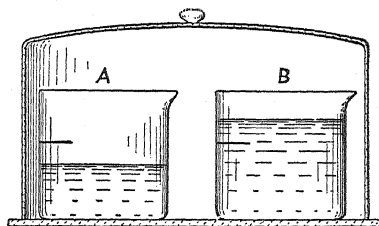
Fig. 12-5. The vapor pressure of a solution of a non-volatile solute in a liquid is lower than that of the solvent. The solute molecules impede the escape of the solvent molecules.

contains calcium chloride as well as water molecules in the mixture and the number of molecules of water which can jump off the surface of the liquid is hence restricted by the occurrence in the surface of the calcium and chloride ions. The solute ions do not, however, impede the return of water to the surface of the liquid. When these two solutions are placed under the bell jar, there may be, say, in one instant 100 molecules of water leaving the surface of the water and 80 molecules of water leaving the surface of the solution while 90 molecules return to the surface in each case. Under these circumstances the volume of water in the beaker will diminish while the volume of the solution will increase.

5. The boiling point of a solution is different from the boiling point of the solvent. For those solutions which are made up of a nonvolatile nonionized solute dissolved in water, the boiling

point is raised 0.52°C . above 100°C ., the boiling point of water, for each gram molecular weight of solute per 1000 grams of water. This is true when the boiling point is measured at 760 millimeters pressure. This is to be expected from the vapor pressure. You will remember that the boiling point of a liquid (or of a solution) is the temperature at which the vapor pressure of the liquid just exceeds the pressure on the liquid. At 100°C ., the vapor pressure of pure water is 760 millimeters. If a solute causes the vapor pressure of the water solution to be lower than 760 millimeters at 100°C ., then it will take a higher temperature to reach this pressure and the boiling point will be higher. On the other hand, if the solute is volatile and causes an increase in the vapor pressure, the boiling point will be lower than that of the solvent.

Fig. 12-6. Vapor pressure of a solution of calcium chloride in water compared to water. Beakers A and B contained equal volumes, A of water and B of calcium chloride in water. Marks on the beakers indicate original volumes. A bell jar was placed over them on a glass plate so that the system might be airtight. Slowly the volume of the water diminished and that of the solution increased. This indicates that water has a higher vapor pressure.



The boiling point of a solution of a nonionized nonvolatile solute can be used to determine the molecular weight of the solute.

6. The freezing point of a solution is lower than the freezing point of the solvent. For nonionized, nonvolatile substances one gram molecular weight of solute dissolved in 1000 grams of water causes a depression of the freezing point of 1.86°C . In other words, a solution which contains one gram molecular weight of solute in 1000 grams of water will freeze at -1.86°C . At 760 millimeters pressure the freezing point of water is 0°C . you will remember.

7. Osmosis. Under (3) it was pointed out that solutions will dialyze through membranes which have pores large enough to permit the solvent and solute molecules to slide through, but small enough to hold back particles which are larger than

ordinary molecules. Some membranes have such tiny pores that only small molecules such as water can pass through while larger molecules such as sugar will either pass through more slowly or not at all. When a solution is separated by such a

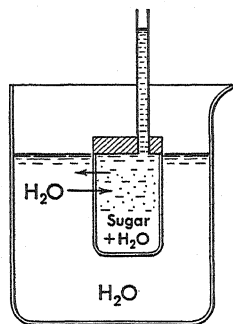


Fig. 12-7. *Osmosis. A sugar and water solution is placed in a cellophane cup and suspended in a beaker of water. The level of the liquid in the tube slowly rises since more water molecules pass into the cup through the membrane than pass out.*

semipermeable membrane from either pure solvent or a solution of different concentration, a change in volume occurs. This phenomenon is called *osmosis*. If, for example, a sack of cellophane is prepared which has such small pores that it will not allow sugar molecules to pass through, and if a solution of sugar and water is placed in the sack and it is hung in a beaker of water, before long it will be noticed that the volume of sugar solution is increasing and the volume of pure water is decreasing. This is an example of osmosis.

This experiment can be explained on the basis of the Kinetic Theory. The molecules in the sugar-water mixture are moving about. Some of the water molecules bump against the cellophane membrane and slide through. When sugar molecules bump against the membrane, they prevent for the moment the passage of water molecules through the membrane. However, on the other side of the membrane there are no sugar molecules and any water which bumps into the membrane may have a chance of sliding through. Therefore, the number of molecules which slide through from the pure water to the solution is greater than the number of molecules which pass in the opposite direction. The volume of the solution increases as water molecules increase on that side of the membrane. The volume of the pure water will decrease since more molecules are moving out of it than are moving in.

This change in volume can be prevented. With a more complicated apparatus arranged so that the pressure on the surface of the solution can be increased without increasing it on the surface of the pure water, the differential passage of molecules can be prevented. By carrying out a series of experiments, gradually increasing the pressure on the solution, the pressure which it is necessary to superimpose on the solution to prevent osmosis will be found. This pressure is called the *osmotic pressure* of the solution.

If the solution had been separated from a sugar solution which was more dilute than it, a change in volume in the same direction would have occurred. The volume of the concentrated solution would have increased and the volume of the dilute solution decreased.

Osmosis is the tendency of a greater number of ions or molecules to cross a semipermeable membrane from a solution concentrated in them to a solution dilute in them. Osmosis is important in the exchange of compounds across biological membranes. The absorption of water and salts by root hairs, the absorption of some nutrients through the wall of the gastro-intestinal tract, the loss of waste materials by cells into the blood stream are all examples of osmosis. However, osmosis does not completely explain the passage of all materials across biological membranes.

A solution which has the same osmotic pressure as a reference solution is called an *isotonic* solution. A solution which has a lower osmotic pressure than the reference solution is called *hypotonic* solution, whereas a solution which has a greater osmotic pressure than the reference solution is called a *hypertonic* solution. In biochemistry and medicine, the reference solution is usually the blood, so an isotonic solution is a solution which has an osmotic pressure equal to the osmotic pressure of the blood. If blood cells are suspended in a solution which is isotonic to the blood, they will retain their original shape. If, however, they are placed in a solution which is hypotonic to the blood, a greater amount of water will pass into the cells than will pass out of the cells, and the cells will swell and rupture. If the cells are placed in a solution which is hypertonic to the blood, more water will pass out of the cells than will pass into the cell, and the cells will shrivel.

There are many examples of osmosis in the field of food preparation. For example it can be demonstrated with two prunes.

Place one shriveled prune into a beaker of pure water and notice that in several hours the prune will swell to a large size so that the skin is smooth. Place the other prune in a concentrated solution of sugar in water and notice that the size of the prune does not change. In the first case a large number of molecules of water are passing through the semipermeable membrane of the skin of the prune into the prune and a small number are passing out. Thus the size of the prune increases. In the second case, the number of molecules of water passing into the prune is equal to or perhaps even less than the number of molecules of water passing out of the prune.

Sprinkle sugar over strawberries and notice how rapidly they shrivel. When the sugar coats the strawberry, it forms on the damp surface a very concentrated solution of sugar in water. The osmotic pressure of this solution is much greater than the osmotic pressure of the solution inside the strawberry. It is hypertonic. Much more water passes out of the strawberry than passes in, and before long, shriveled strawberries are in a pool of juice. (The fact that other substances than water pass through the skin of the strawberries is evidenced by the flavor and color of the juice.)

Can plums or pickles in a heavy syrup or heavy vinegar, sugar, and spice mixture and notice that they shrivel. Or can them in pure water and notice how they enlarge and how the plums rupture.

The fact that the freezing points and the boiling points of solutions of nonvolatile, nonionized compounds in water, or in any other solvent, are functions of the number of gram molecular weights of solutes dissolved, gives a method for calculating:

1. The freezing points or boiling points of solutions of known concentrations.
2. The molecular weights of unknown substances which are nonvolatile and nonionized.
3. The amount of substance which must be added to a solution in order to achieve a definite boiling point or freezing point. The freezing points and boiling points of solutions are defined in terms of *molal* solutions. *A molal solution is one which contains one gram molecular weight of solute in 1000 grams of water.* (This is different from the *molar* solution which is discussed in Chapter 15.) The *freezing point* of a solution of a nonionized non-

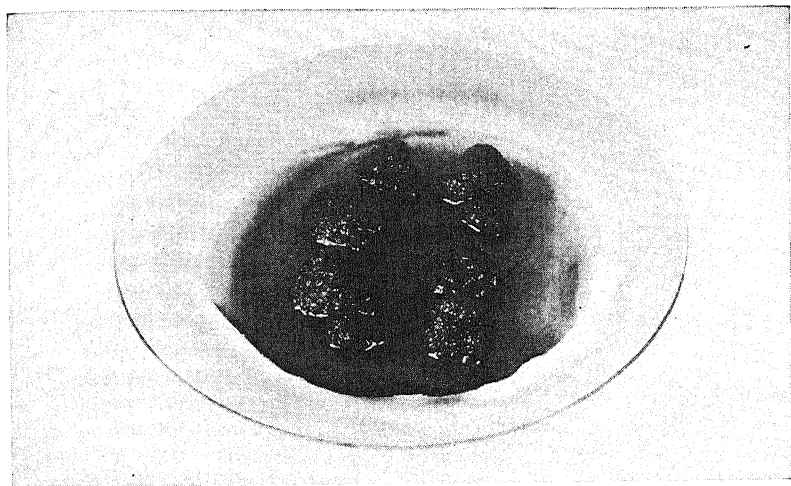


Fig. 12-8. Osmosis. Strawberries were covered with sugar and allowed to stand for several hours. Through the effect of osmosis, more water passed out of the berries than passed in. They were soft shriveled berries in a pool of juice.

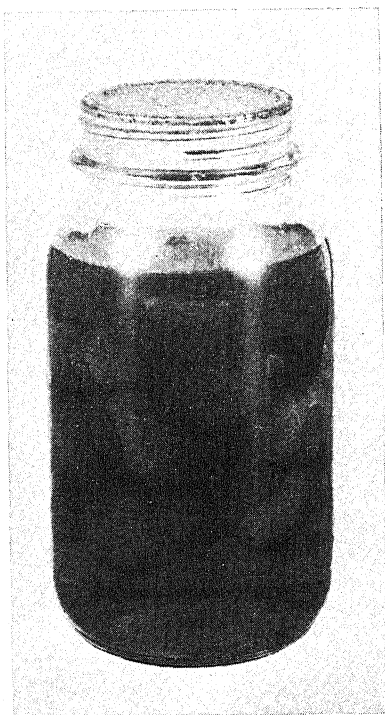


Fig. 12-9. Osmosis. These plums were canned in a hypotonic solution. More water passed into the plums than passed out. Every one is ruptured.

volatile solute is depressed 1.86°C . for each gram molecular weight dissolved in 1000 grams of water. The boiling point of a solution of a nonionized nonvolatile solute is raised 0.52°C . at 760 millimeters pressure for each gram molecular weight of solute dissolved in 1000 grams of water.

Suppose that you wish to calculate the freezing point of a solution of alcohol and water. If the amount of alcohol and the amount of water is known, you can calculate the freezing point.

PROBLEM: Calculate the freezing point of a solution which contains 50 grams of alcohol, $\text{C}_2\text{H}_5\text{OH}$, in 1000 grams of water.

ANSWER: The gram molecular weight of $\text{C}_2\text{H}_5\text{OH} = 46$ grams ($24 + 6 + 16 = 46$). One gram molecular weight of alcohol (46 grams) dissolved in 1000 grams of water will have a freezing point lowering of 1.86°C .

$$\begin{aligned}\frac{50 \text{ g.}}{\text{GMW}} &= \frac{x^{\circ}}{1.86^{\circ}} & \frac{50 \text{ g.}}{46 \text{ g.}} &= \frac{x^{\circ}}{1.86^{\circ}} \\ x^{\circ} &= 2.02^{\circ}, \text{ depression of freezing point} \\ 0^{\circ} - 2.02^{\circ} &= -2.02^{\circ}\text{C.}, \text{ freezing point}\end{aligned}$$

PROBLEM: Calculate the boiling point of a solution containing 25 grams of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, dissolved in 100 grams of water.

ANSWER: First calculate the number of grams of glucose dissolved in 1000 grams of water.

$$\begin{aligned}\frac{x \text{ g. glucose}}{25 \text{ g. glucose}} &= \frac{1000 \text{ g. H}_2\text{O}}{100 \text{ g. H}_2\text{O}} \\ x &= 250 \text{ g.}\end{aligned}$$

The gram molecular weight of glucose is 180 ($72 + 12 + 96 = 180$).

$$\begin{aligned}\frac{250 \text{ g. glucose}}{180 \text{ g. (GMW)}} &= \frac{y^{\circ}}{0.52^{\circ}} \\ y &= 0.72^{\circ} \text{ rise in boiling point} \\ 100^{\circ} + 0.72^{\circ} &= 100.72^{\circ}\text{C. boiling point.}\end{aligned}$$

PROBLEM: Calculate the gram molecular weight of a substance if a solution containing 3 grams in 25 grams of water has a freezing point of -3.72°C .

ANSWER: First calculate the number of grams of solute dissolved in 1000 grams of water.

$$\frac{x \text{ g.}}{3 \text{ g.}} = \frac{1000 \text{ g. H}_2\text{O}}{25 \text{ g. H}_2\text{O}}$$

$$x = 120 \text{ g. in 1000 g. H}_2\text{O}$$

120 grams dissolved in 1000 grams of water has a freezing point of -3.72°C .

$$\frac{120 \text{ g.}}{\text{GMW}} = \frac{3.72^\circ}{1.86^\circ}$$

$$\text{GMW} = 240 \text{ g.}$$

PROBLEM: Calculate the number of grams of methyl alcohol, CH_3OH , which must be added to 250 grams of water to prevent it freezing above -10°C .

ANSWER: Calculate the gram molecular weight of the CH_3OH ($12 + 4 + 16 = 32$). One gram molecular weight (32 grams) dissolved in 1000 grams of water has a freezing point depression of 1.86° .

$$\frac{x \text{ g.}}{32 \text{ g. (GMW)}} = \frac{10^\circ}{1.86^\circ}$$

$$x = 172 \text{ g.}$$

172 grams dissolved in 1000 grams of water will depress the freezing point to -10°C .

$$\frac{y \text{ g.}}{172 \text{ g.}} = \frac{250 \text{ g. H}_2\text{O}}{1000 \text{ g. H}_2\text{O}}$$

$$y = 43 \text{ g. must be dissolved in 250 g. H}_2\text{O}$$

Crystallization

Crystallization from solution is important in two general fields of food preparation, sugar cookery and the preparation of frozen desserts. Briefly this phenomenon of crystallization from solution, some of the factors which influence it, and applications in food preparation will be studied.

You will remember that a crystal of a pure substance is composed of a closely packed mass of molecules or ions, arranged in a very definite pattern (see Solids, p. 89). The crystal of sodium chloride is composed of sodium and chloride ions arranged alternately in a lattice, which yields a cubical

structure to the crystal. When a crystal is formed in a solution, molecules or ions are deposited in a regular lattice to build up this crystal. Crystallization from solution can occur only if the solution is slightly or markedly supersaturated. The size of the crystals produced will depend upon two factors: (1) the rate of formation of nuclei about which crystals grow and (2) the rate of crystallization or the rate of the growth of crystals about these nuclei. If the crystals are formed from a solution under conditions in which only two nuclei are formed, no matter whether the rate of crystallization is slow or fast, the size of the crystals produced will be large. If, on the other hand, the rate of formation of nuclei is very rapid, then whether crystallization is slow or fast, there will be many crystals and they will all be relatively small. Both the rate of crystallization and the rate of formation of nuclei are influenced by numerous factors.

1. *Nature of the crystallizing substances.* Some substances do not have the ability to produce very large crystals. They produce nuclei rapidly and grow from these many centers. Quite the reverse is true of some other substances.

2. *The concentration of the solution.* Crystallization from solutions in which the extent of supersaturation is great results in a very rapid rate of crystallization. Usually it also results in a very rapid formation of nuclei so that the final solid is composed of many small crystals.

3. *Temperature.* In general, small crystals are produced at low temperatures and larger crystals at high temperatures.

4. *Agitation.* Stirring fosters the formation of many small crystals. Probably when you stir a solution, you break off many nuclei from the crystals already formed. Also agitation will bring supersaturated solution in contact with crystals. In a very still solution there would be a relatively small zone of saturated solution around each crystal and it would take some time for more solute to diffuse into that area.

5. *Impurities.* Impurities which are similar in chemical structure to the material which is being crystallized will occasionally be deposited on the crystal and afterwards prohibit or impede further growth on that side of the crystal. For example, glucose interferes with the crystallization of sucrose. Other impurities may interfere with crystallization, merely by coating the crystal. For example, fat is not actually in solution, but if it is present

in the mixture, it will interfere with the crystallization of sucrose by coating the crystal.

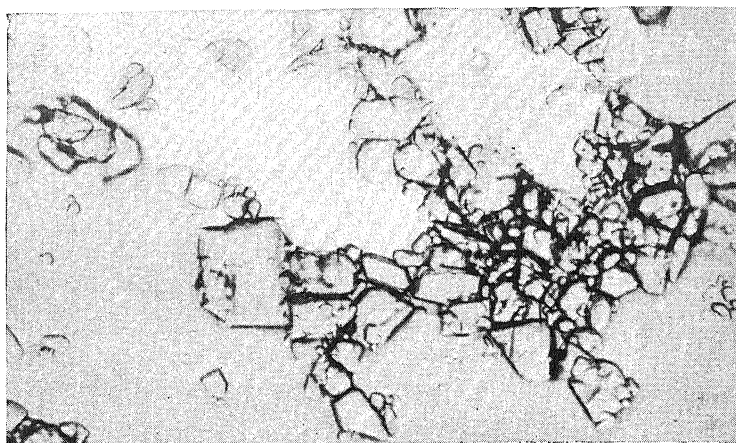
If you introduce a crystal into a supersaturated solution in order to start crystallization, it is called *seeding*. In preparing synthetic organic chemicals, this is frequently resorted to in order to produce the crystalline material. In sugar cookery procedures are used to avoid seeding. The crystallization must not take place until the cook is ready for it. Crystals are carefully washed from the sides of the pan so that they will not fall into the hot supersaturated solution and, by inducing crystallization at a high temperature, produce large crystals.

Applications *Sugar cookery.* A sugar cookery recipe for simple fondant and the variations in recipes will illustrate principles of crystallization. In preparing fondant, the goal is to produce a product with extremely small crystals so that it will feel velvety to the tongue. In the following recipes attempts are made to keep the crystals small.

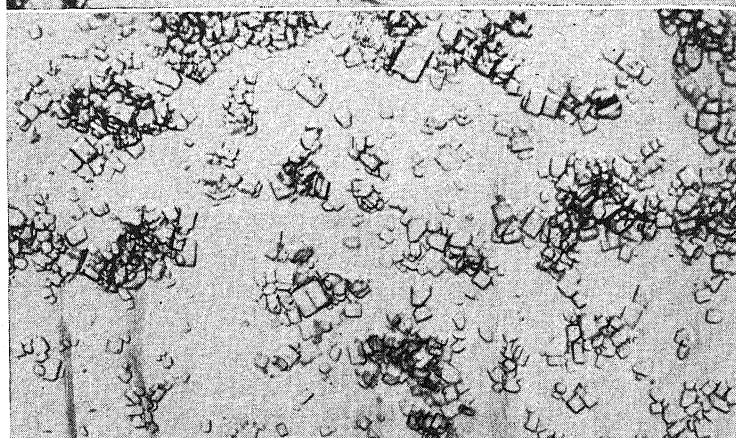
Recipe: Add one cup of sugar to one-half cup water. Stir carefully with warming until the sugar is dissolved. Cover the pan and allow to boil gently until the steam has washed the crystals on the side of the pan down into the solution, or dampen a cloth wrapped on a fork and wash all crystals into the solution. Uncover and boil the solution gently to a temperature of 113°C . Avoid stirring. The thermometer should be arranged so that the bulb is in the solution, but so that it does not touch the bottom or side of the pan. When the temperature reaches 113°C ., turn off the heat and allow the mixture to cool to 40°C . Then beat until it begins to thicken. Scrape out onto a platter and knead.

In this recipe precautions are taken to remove every crystal which might seed the solution while it is cooling and is supersaturated. At 40° the solution will be very supersaturated, and the formation of nuclei or crystal centers will be very rapid. When you stir it at this cool temperature, both the stirring and the concentration will tend to produce many small crystals. It is possible to produce a velvety, high quality fondant with this recipe. Unfortunately, the candy tends to become grainy on standing.

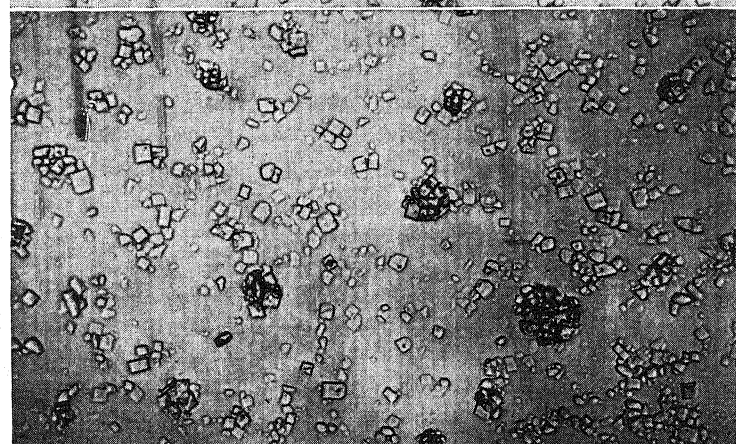
The fondant is a mixture of very small crystals and a small amount of a saturated solution of sugar (its chemical name is



1.



2.

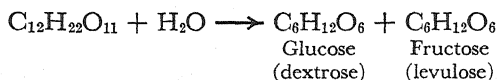


3.

sucrose) and water. The saturated solution is in dynamic equilibrium with the crystals. On standing, sugar molecules in solution are continually depositing on the crystals already formed and some of the sugar molecules on the crystals are continually dissolving. It is the smallest crystals which eventually disappear from the mixture and the largest crystals grow even bigger.

Many recipes have been developed for fondant in which foreign substances are introduced which prevent or minimize the development of graininess. The addition of corn syrup, which contains dextrans, maltose, and glucose, will make it easier to produce small crystals in the first place and will prevent the growth of large ones as the fondant stands. Of course the same precautions must be followed in preventing crystals from seeding the cooling solution. On stirring sucrose (sugar) crystals are formed, but glucose, maltose, or dextrans deposit or coat the crystals and they do not grow so large. These "foreign" carbohydrates have a similar effect when the candy stands.

Still other recipes have been developed which use a substance to bring about a chemical change in part of the sucrose during cooking and by so doing introduce a "foreign" carbohydrate. In the presence of acid, sucrose is hydrolyzed to glucose and fructose.



Acid is introduced by adding a teaspoon of vinegar or a quarter teaspoon of cream of tartar (potassium acid tartrate). During the cooking, small amounts of glucose and fructose will be



Fig. 12-10. Sugar crystals. (1) Sugar-water syrup cooked to 113° C. and beaten immediately until stiff enough to knead. (2) Portion of same syrup, but cooled to 40° C. and then beaten. The crystals are much smaller when the syrup is cooled before beating. (3) Divinity beaten until a piece dropped from a spoon holds its shape. The crystals are small since egg white retards crystallization. Magnification approximately 200 times. (Reproduced by permission from Experimental Cookery, 3rd Ed., by B. Lowe, published by John Wiley and Sons, Inc., 1943.)

produced from the sucrose. These other carbohydrates will then interfere with crystallization when the cooled solution is stirred and they will also prevent the growth of large crystals in the fondant on standing. The acid is faintly discernible in the candy, but adds a pleasant slightly tart taste.

Look over other sugar cookery recipes for fudge, boiled frosting, seven-minute frosting, divinity, etc., and try to pick out the ingredients and the procedures which minimize the size of the sugar crystals.

Frozen mixtures. In a frozen mixture ice crystals are produced and in order that the product may be high quality it is likewise necessary that these crystals be very small and therefore velvety to the tongue. The most successful frozen mixtures are prepared by churning a mixture which has been well cooled, preferably supercooled. With an efficient freezer, the dashers will churn a good deal of air into the mixture. These bubbles of air will make the mixture light and will interfere with the growth of ice crystals. In a mechanical refrigerator where it is difficult to have much churning except by removing the mixture from the refrigerator and beating it, high quality frozen mixtures are very difficult to prepare.

It is possible with a good freezer to obtain very small crystals and therefore a pleasing consistency with simple fruit juice and sugar mixtures. However the "ice" becomes grainy on standing. Most mixtures for frozen desserts contain a number of other ingredients which interfere with the formation of ice crystals and keep them small.

Look over the recipes for ice creams, sherbets, mousses, marlows, etc., and pick out the ingredients which will coat the crystals and prevent the growth of large ice crystals. In these frozen desserts the ingredients which have this effect are colloidally dispersed in the mixture. In homemade ice cream, cream which contains emulsified butterfat is one of the favorite ingredients for keeping the crystals small. It also adds a delightful richness and tends to mellow flavors. Cooked egg in custard mixtures, whipped egg white in sherbets, gelatin, and cooked starch are occasionally used. None of these substances is effective enough to produce a smooth frozen mixture unless some churning is used in the preparation. In a mechanical refrigerator even though the mixture is removed and beaten when it is partially frozen, ice crystals tend to be large and the mixture

grainy. In a freezer, with a dasher, the product is usually smooth and creamy. Marlows which are made by dissolving a number of commercial marshmallows in milk or cream, flavoring, and then freezing, are usually successful in a mechanical refrigerator. The marshmallows contain a large amount of gelatin and gum which hinder to a small extent the development of ice crystals. The air which is trapped in the marshmallows and which is not all released when they are dissolved is effective in preventing large crystals. Most of the package mixes for home-made ice cream contain gums, starches from various cereals, gelatin, or a mixture of these substances.

All the colloidal agents which tend to inhibit crystal growth during freezing have a second effect which is not concerned with crystallization, but which is important in the success of the product. They all have the ability to form gels, and they give the melting dessert considerable body. The quantity must be carefully regulated, since most people do not like a frozen dessert which on melting is only semiliquid.

NEW TERMS

Solute, solvent, heat of solution, concentrated solution, dilute solution, saturated solution, supersaturated solution, dialysis, osmosis, osmotic pressure, isotonic solution, hypotonic solution, hypertonic solution.

QUESTIONS

1. Give one example of each type of solution and explain why each is a true solution. Name the solute and the solvent.
2. Explain why the temperature falls when solid ammonium chloride dissolves in water.
3. Explain why the temperature rises when concentrated sulfuric acid is added to water. Is this a physical or chemical action?
4. How can you distinguish a saturated, a supersaturated, and an unsaturated solution? If you have a solution of sodium thiosulfate in water, how can you go about showing whether the solution is saturated or not?
5. Why must the osmotic pressure of a solution be carefully regulated before it is injected into the blood stream?
6. Calculate the freezing point of a solution which contains 14 grams of urea, CH_4ON_2 , dissolved in 20 grams of water. What is the boiling point?

7. Calculate the molecular weight of a compound of which 5 grams are dissolved in 100 g. of water. The freezing point is depressed 1.55°C .
8. Calculate the molecular weight of compound x , if a solution containing 1.92 grams in 25 g. of water freezes at -1.488°C .
9. How much alcohol ($\text{C}_2\text{H}_5\text{OH}$) must be added to 100 grams of water to lower the freezing point to -10°C ?
10. How do you account for the fact that the fudge which takes a long time to beat is usually the smoothest?
11. For what purpose is corn syrup added to chocolate syrup sauces (non-crystalline)?
12. If large amounts of corn syrup were added to fudge, what effect might be produced?
13. Why does a bottle of warm ginger ale "fizz" over?
14. Why does a water solution of alcohol boil below 100°C . and one of sugar above 100°C .?
15. When can the temperature of a boiling solution be used as an end point in candy making?
16. Under what conditions may it be true that an ice-salt mixture cannot freeze a frozen dessert?
17. What effects would you expect if slices of apple were cooked in a concentrated sugar syrup?
18. Explain why one becomes thirsty after eating ham.
19. When glycerine is added to a supersaturated sugar solution, the crystallization of the sugar may be greatly hindered. The resultant sugar crystals are much smaller than those which separate from a supersaturated solution of pure sugar. Explain.
20. A recipe for hard candy is changed from a solution of all cane sugar to a solution of one-half cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) and one-half corn sugar ($\text{C}_6\text{H}_{12}\text{O}_6$). How will this affect the temperature of the solution at the brittle stage?
21. A saturated solution of sugar is cooled without crystallization taking place. What is the state of saturation at the lower temperature?
22. What is the effect of churning on the fineness of an ice cream? Why is it necessary to use heavier cream (higher percentage of fat) when an ice cream is made without churning, as in a mechanical refrigerator?
23. How much glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) must be added to 500 g. of water to raise the boiling point at 760 millimeters to 108°C .?
24. A car radiator holds 14 quarts. Calculate the amount of wood alcohol (CH_3OH) which must be added to each quart of water to prevent the solution from freezing above 10°F . Calculate for glycol ($\text{C}_2\text{H}_4(\text{OH})_2$).

Ionization

Michael Faraday (1791–1867), great English physicist and chemist, developed some of the fundamental ideas of electricity. Among other things, he studied the conductivity of solutions. He noticed that an electric current will pass through some solutions, will pass with difficulty through others, and will not pass through some. He did not understand the reason for this difference, but he devised the terms *electrolyte* and *nonelectrolyte* to distinguish solutions capable of conducting electricity from those which cannot. He also at this time coined the term *ion* to designate that part of the solution which conducted the current. He did not understand what an ion was or why the solution did conduct the current.

Conductivity in solutions may be demonstrated by a simple apparatus. Two wires, or electrodes, connected to an electric circuit are placed in a solution. A light bulb is placed in the circuit so that if the electrodes touch one another the light bulb will glow — electricity will flow through the circuit. If when the electrodes are placed in the solution and are

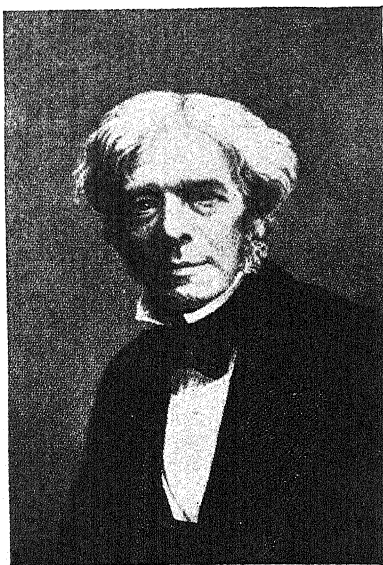
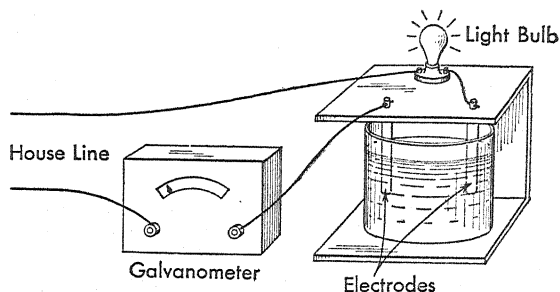


Fig. 13-1. Michael Faraday. (Courtesy of Journal of Chemical Education.)

arranged so that they do not touch the light bulb glows, the solution is conducting the current.

Fig. 13-2. Apparatus for testing the conductivity of solutions. Current flows from the house line through the galvanometer which gives a comparison of the conductivity, through the solution, and finally through the light bulb. The glowing of the bulb is a rough measure of the amount of current flowing through the solution.



Almost fifty years later, Arrhenius on investigating the freezing points and boiling points of solutions, noticed that the freezing points and boiling points of those solutions which Faraday called electrolytes showed a much greater variation from the freezing points and boiling points of the solvent than did solutions of non-electrolytes. For example, the freezing point of one gram molecular weight of sugar in 1000 grams of water is 1.86° below the freezing point of water, while the freezing point of one gram molecular weight of sodium chloride in 1000 grams of water, an electrolyte, is -3.36°C .



Fig. 13-3. Arrhenius (Courtesy of Journal of Chemical Education.)

Lowering of the Freezing Point of Water

<i>Solute</i>	<i>Character</i>	<i>Formula</i>	<i>Lowering produced in 1000 g. of water by 1 GMW of compound</i>
Sugar	Nonelectrolyte	$C_{12}H_{22}O_{11}$	1.86°
Alcohol	Nonelectrolyte	C_2H_6O	1.83°
Urea	Nonelectrolyte	$CO(NH_2)_2$	1.86°
Hydrogen chloride	Electrolyte	HCl	3.61°
Nitric acid	Electrolyte	HNO_3	3.59°
Potassium hydroxide	Electrolyte	KOH	3.44°
Sodium hydroxide	Electrolyte	NaOH	3.43°
Sodium chloride	Electrolyte	NaCl	3.36°

After studying the freezing points and boiling points of many solutions, Arrhenius at last concluded that a solution which contains one gram molecular weight of an electrolyte contains more particles in it than a solution which contains one gram molecular weight of nonelectrolyte. You will remember that two gram molecular weights of sugar dissolved in 1000 grams of water has a freezing point of -3.72°C .

What accounts for these extra particles present in solutions of electrolytes? Why is it that one gram molecular weight of sodium chloride has more particles in it than one gram molecular weight of sugar? Arrhenius developed the Theory of Ionization and found the answer to these questions and other observations.

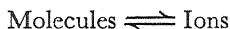
Assumptions of Arrhenius' Theory of Ionization

1. In solution, electrolytes form ions which are independent particles.
 2. There is an electric charge on ions, either positive or negative. They differ in this from atoms.
 3. The total numbers of positive and of negative charges are equal.
 4. Nonelectrolytes do not ionize in solution.
 5. There is an equilibrium between ionized and nonionized particles.
- Arrhenius believed that there was a dynamic equilibrium between molecules and ions in each solution. Today it is believed that this is true only of weak electrolytes. Strong electrolytes appear to exist as ions even in the solid state. You will remember that x-ray analysis study indicates that the crystal lattice of many solids is made up of

ions arranged in definite patterns. Not all solids are strong electrolytes, but those solids which are strong electrolytes are completely ionized in the solid state.

6. Debye and Hückel have presented an addition to Arrhenius' theory. Strong electrolytes are 100% dissociated. In solutions of considerable concentration, these ions of strong electrolytes will not be completely independent particles. Some positive ions will have an attraction for some negative ions. But no undissociated molecules exist.

Weak electrolytes appear to be substances intermediate between strong electrolytes and nonelectrolytes. In solution, there is equilibrium between molecules which are not ionized and ions. Sometimes the equilibrium point is far on the side of the molecules, sometimes far on the side of the ions.



This assumption of Arrhenius' theory applies only to weak electrolytes.

Strong electrolytes are in general the following substances:

1. Mineral acids such as nitric, HNO_3 , sulfuric, H_2SO_4 , and hydrochloric, HCl .
2. Hydroxides except ammonium hydroxide, NH_4OH .
3. All salts.

These generalizations are not true in all cases, but they will give you a simple differentiation of substances.

Weak electrolytes are:

1. Carbon acids; phosphoric acid, H_3PO_4 ; sulfurous acid, H_2SO_3 .
2. Ammonium hydroxide, NH_4OH .

Why do solutions of strong electrolytes have the ability to conduct a current readily? If two electrodes connected to an electric circuit are placed in a solution, one electrode will have a strong negative charge on it and the other electrode will have a strong positive charge on it. Since opposites attract one another, negative ions will be attracted to the positive electrode. At the positive electrode, the negative ions will lose electrons and undergo oxidation. At the negative electrode the positive ions will gain electrons and undergo reduction. For example, in a solution of hydrochloric acid in water there are positive hydrogen ions and negative chloride ions. When electrodes

attached to an electric circuit are introduced into the solution the hydrogen ions are attracted to the negative pole and the

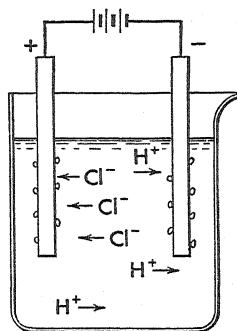
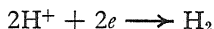


Fig. 13-4. *Electrolysis of HCl. The hydrogen ions are attracted to the cathode and discharge to form bubbles of H_2 , while the chlorine ions are attracted to the anode, lose electrons, and form chlorine gas.*

chloride ions are attracted to the positive pole. The hydrogen ions pick up electrons at the negative pole and form free hydrogen molecules.



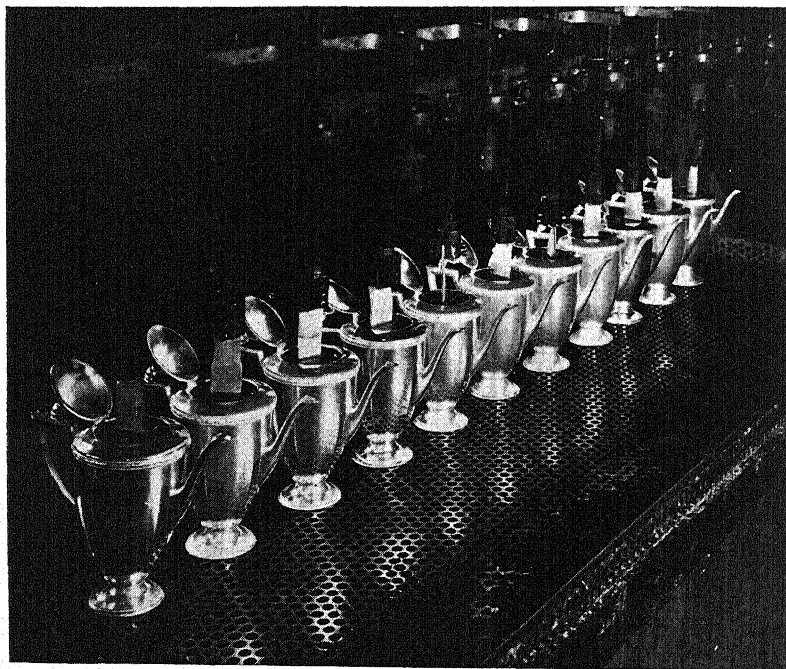
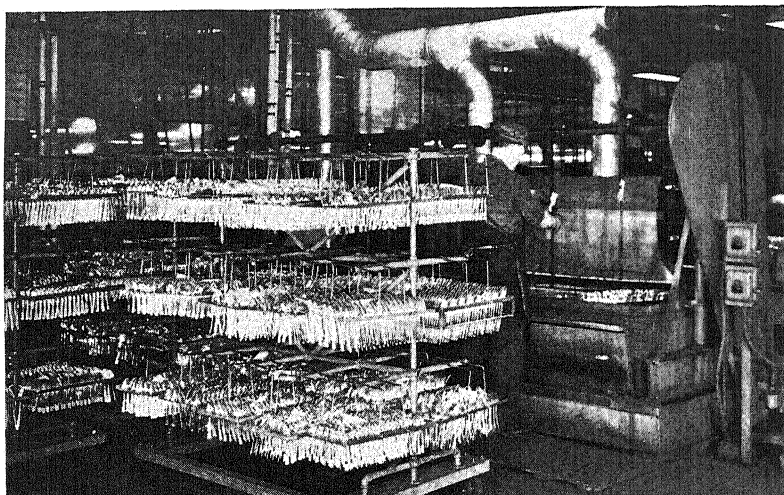
At the positive electrode the chloride ions lose electrons



This is called an *electrolytic reaction*, and the system made up of the solution with the two electrodes in place is called an *electrolytic cell*.

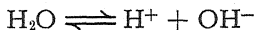
Faraday named the negative electrode in an electrolytic cell the *cathode*, and the positive electrode the *anode*. Since the positive ions in a solution migrate to the cathode, they are called *cations*, and since the negative ions migrate to the positive pole, they are called *anions*.

Electrolytic Reactions Any endothermic reaction which occurs in an electrolytic cell is called an electrolytic reaction. The energy needed by the reaction is supplied by the electricity. You will remember the electrolysis of water in which a dilute solution of sulfuric acid is placed between two electrodes. Hydrogen bubbles off of one electrode and oxygen off of the other. This is a typical electrolytic reaction. You will also remember the Electromotive Series of Elements in which the elements which lose their electrons most readily are placed at the top of the series, hydrogen is midway down, and the elements which lose their electrons with difficulty are at the bottom of the



series. This Electromotive Series of Elements is useful in electrolytic reactions as well as in replacement reactions. The ions of elements which lose their electrons easily will pick up electrons with difficulty. The ions of elements which lose their electrons with difficulty will pick up electrons readily. Radicals may also be included in this Electromotive Series. Thus silver ion picks up electrons readily while free silver loses them to form silver ion with difficulty. Sodium ion does not pick up electrons readily.

When a dilute solution of sulfuric acid is electrolyzed to produce hydrogen and oxygen, the positive hydrogen ions in the solution collect at the cathode, the negative electrode, while the negative ions collect at the anode, the positive electrode. In a dilute solution of sulfuric acid in water, there will be two types of negative ions. Sulfate ions, $\text{SO}_4^{=}$, and a few hydroxyl ions, OH^- , are produced from the very slight ionization of water.



At the cathode, hydrogen ions will accept electrons and form hydrogen molecules and escape as hydrogen gas.



At the anode sulfate ions and hydroxyl ions will accumulate. Sulfate ions are not readily discharged. They do not lose electrons with ease. The hydroxyl ions, on the other hand, are more readily discharged and therefore lose electrons.

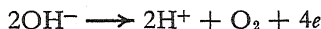


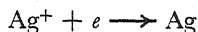
Fig. 13-5. Silver plating flatware. The bodies of relatively inexpensive metal are hung in racks and dipped into the electroplating solution. Here they are connected to an electric circuit where they become negatively charged as the cathode. The silver ions move to the cathode, pick up electrons, and are deposited. (Courtesy of Oneida Ltd.)

Fig. 13-6. Silver plating the inside of coffee pots. The pot acts as the cathode on which silver ions pick up electrons and are deposited. The silver anode from which silver ions are liberated dips into the electroplating solution which fills the pots. (Courtesy of Oneida Ltd.)

Hydrogen gas is liberated at the cathode while oxygen gas is liberated at the anode.

Plating reactions are all electrolytic reactions. You are familiar with objects which are silver plated, chrome (chromium) plated, and nickel plated. In these objects the plated metal is deposited in a hard, lustrous even coat which does not peel or blister. The composition of the plating solution, the amount of electricity (current density), and even the presence of other ions influence the characteristics of the plate. In forming the plate, a metallic base is dipped into a solution, containing the ion of the metal to be plated, and is attached to an electric circuit in such a way that it becomes the cathode. When the current is turned on, the metallic base becomes negatively charged and attracts the positive metal ions. They pick up electrons from the base and are deposited as free metal molecules.

Silver-plated flat ware and hollow ware is usually composed of a metallic base made of some white metal alloy such as German silver (copper 52 per cent, zinc 26, nickel 22). Occasionally it is copper or a copper alloy. The advantage of the white metal is that when the silver wears off in spots, the base does not show through noticeably. The metallic base is placed in the electrolytic cell as the cathode. The plating solution is composed of silver cyanide and potassium cyanide. When the current passes through the solution, the silver ions are deposited on the base.



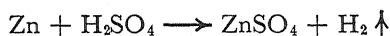
The concentration of the silver ion in the plating solution is maintained by using a bar of silver for the anode. Here the free silver loses electrons and forms silver ions.



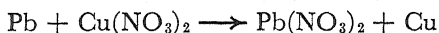
For every ion deposited on the cathode, another ion is formed at the anode. Most silver is plated several times and you will see that it is marked "double plate" or "triple plate." The thickness of the final plate depends, of course, not only on the number of times it is plated but also on the thickness of the plate laid down during each plating. The fact that a fork or bowl is "triple plate" does not necessarily insure that it will have a

thicker coat of silver than one which is marked "double plate." Silver plate is cheaper than "sterling silver" because most of it is composed of the relatively cheaper metal which forms the base. "Sterling" is flat or hollow ware which is made of the silver alloy containing 92.5 per cent silver and 7.5 per cent copper, and it is the same throughout.

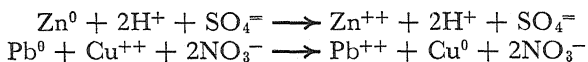
Replacement Reactions Let us go back to replacement reactions and study them now in the light of the Theory of Ionization and the gain and loss of electrons. A free element will react to form a compound and replace a positive ion if the free element is above the positive ion on the Electromotive Series chart. Thus zinc will react with sulfuric acid,



Lead will replace copper in copper nitrate.



If these reactions are written as *ionic reactions*, it will be seen that the reaction involves a loss and gain of electrons by the metals.



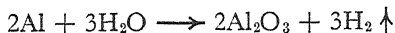
In the first reaction, zinc has lost two electrons to the hydrogen ions. In the second reaction lead has lost two electrons to the copper ion.

Many of the reactions which have been studied are in reality reactions of ions. The ionization of these substances shows clearly what type of reaction has occurred.

In replacement reactions the chemical change is always the loss of electrons by the free metal to a metallic ion. Go over some of the replacement reactions which have been studied and study them from the point of view of gain and loss of electrons.

Pots and pans. The pots and pans which you use about the home are composed of aluminum, iron, copper, or chromium. Frequently they are not pure metals, but alloys. The effects on these metals of water, of hot water, and of the dilute acid solutions such as are frequently encountered in food preparation will be studied. (The addition of a small amount of another metal to produce the alloy may change the reaction of the product.)

Aluminum is rather high on the Electromotive Series and hence shows considerable reactivity. In other words, it loses electrons with ease to form aluminum ions. In the presence of hot water, aluminum will react to produce hydrogen in small amounts.



The aluminum oxide is deposited on the sides of the pan as a grayish white film when water is boiled. This film adheres

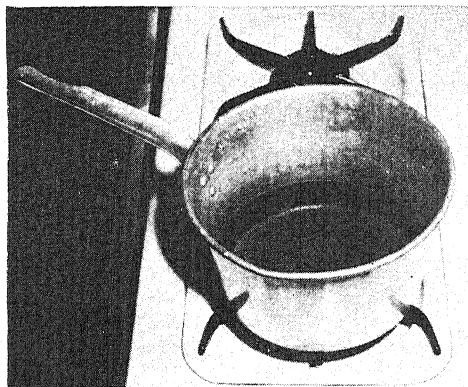
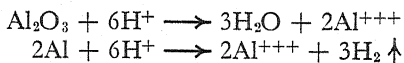
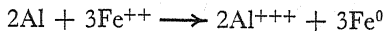


Fig. 13-7. Darkening of an aluminum pan from contact with a food which contained small amounts of iron salts. Since aluminum is above iron on the Electromotive Series Chart, it replaced the iron in the salt and finely divided iron was deposited on the side of the pan. When an acid food is cooked in this pan, the iron will dissolve since it is above hydrogen in the Electromotive Series Chart, and the iron will be eaten in this food.

tightly and diminishes the amount of reaction between the aluminum and water. You will notice this film of aluminum oxide deposited on the pan after boiling with water. Acid foods such as tomatoes have a relatively low concentration of acid, and the acid is a weak acid. The hydrogen ion concentration is low, and the solution reacts very slowly with free aluminum. However, these acids will dissolve the aluminum oxide film.



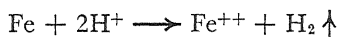
With foods which contain an appreciable amount of iron, a black deposit is observed on the side of the aluminum pan. This is free iron which has replaced aluminum.



All these reactions occur more rapidly at higher temperatures. The fear of poisoning by aluminum dissolved in food from the

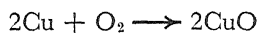
above reactions was held by many people in the early days of the use of aluminum utensils. Even today you will occasionally meet an individual who is afraid to use an aluminum pan. A great number of experiments were devised by which experimental animals were fed large quantities of aluminum ion, far in excess of the amount which might occur in foods from the solution of aluminum during cooking. Animals were studied for generations in attempts to test this possible toxicity. All findings were negative. No animal was ever poisoned. Of course before they ever touch an aluminum pan many foods contain considerable quantities of aluminum in the raw state since the soil contains high amounts of aluminum. There is now little doubt that aluminum is a nontoxic element.

Iron is below aluminum in the Electromotive Series and reacts with hot water only slowly to produce the oxide. It will react in acid solution with the hydrogen ion of the acid to produce iron salts.

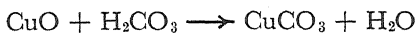


Ferrous and ferric ions have a strong metallic flavor that are very undesirable in foods. Therefore acid foods should not remain in contact with iron vessels longer than is necessary for the cooking operation. Rust cannot be left on an iron pan or the oxide will dissolve in an acid food and develop a strong metallic flavor.

Copper pans do not react with hot water since copper is below hydrogen in the Electromotive Series, nor do they react with acid solutions. But copper very rapidly oxidizes in the air to form copper oxide, CuO .



Then in the presence of moisture and carbon dioxide, green copper carbonate is formed.



Both copper oxide and copper carbonate will react rapidly with the acid in foods to produce a strong metallic flavor. The housewife who uses copper pans must be sure that all the green copper carbonate and the black copper oxide are scoured off before the pans are used in cooking. A hundred years ago many American

women used copper pans, and it took a great deal of scouring and scraping to keep the copper gleaming. It is not surprising that the use of copper pans has passed out of vogue.

Buckets are galvanized iron, that is, the body of the bucket is iron which has been dipped in zinc. This is called *galvanized*. If a solution or water is placed in the bucket, the metal with which it comes in contact is zinc. Zinc is high in the Electromotive Series and hence an acid solution will react rapidly with it. Galvanized iron is not suitable for cooking utensils.

"Tin cans" are made of iron covered with tin. When the can is opened the layers are cut through and the iron is exposed.

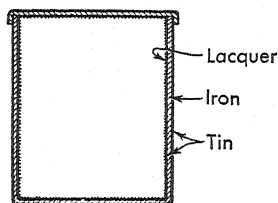
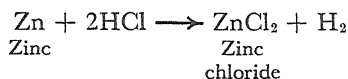


Fig. 13-8. Diagram of a "tin can" made of iron and coated with tin. The inside is usually lacquered.

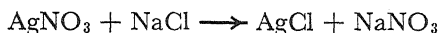
Food may come in contact with either iron or tin. The fact that the can is opened will not affect the speed of the reaction by which acid foods dissolve tin or iron. Many housewives have a fear of storing food in open tin cans. Most cases of food poisoning are not the result of the introduction of metal ions into the food, but rather is the result of a bacterial action. If pathogenic organisms fall into the food and grow there, the food containing the bacteria may be harmful when introduced into the body. When a tin can is opened, the food and the can are absolutely sterile. If the food is poured out into a dish or pan it is contaminated with bacteria. (A pathogenic bacterium is one which causes sickness.) The tin can is a safer place to store the food than a bowl which has bacteria on it. If food is stored for a long period of time in a tin can, the exposed iron may rust and drop into the food, causing a strong metallic flavor. If a food reacts with tin, it will react while it is in the unopened tin can. Most cans which contain reactive foods are coated with lacquer so that the food does not come in contact with the tin.

Reactions Which Go to Completion Some chemical reactions go to completion. Analysis of the reaction mixture shows that during the course of the reaction all the reactants have

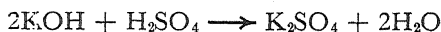
disappeared and nothing remains but the products. Reactions between electrolytes which go to completion are those in which one of the products is (1) a gas, (2) difficultly soluble, or (3) poorly ionized. If zinc is dropped into dilute hydrochloric acid, it will disappear (provided there is sufficient hydrochloric acid), and hydrogen will be given off until all the zinc is gone.



Silver chloride, AgCl, is an example of a difficultly soluble substance. When it is formed by a reaction, that reaction goes to completion.



Water is an example of a compound which is poorly ionized and which is frequently formed in a chemical reaction from electrolytes. When this occurs, the reaction may be considered to go to completion.



When it is said that none of the reactants will be present after the reaction has occurred, laboratory conditions in which the proper molecular proportions of reactants are used are indicated. This would mean that for the reaction of zinc and hydrochloric acid, 1 gram molecular weight of zinc is used for each 2 gram molecular weight of acid. Or in the next reaction 1 gram molecular weight of silver nitrate is used for each gram molecular weight of sodium chloride. In the reaction of potassium hydroxide and sulfuric acid the ratio is 2 gram molecular weights of potassium hydroxide for each gram molecular weight of sulfuric acid. These weights must be very accurately measured. Usually when you carry out a reaction in the laboratory, approximate quantities of materials are used. Thus you add to your test tube approximately 5 ml. of silver nitrate solution and approximately an equal volume of sodium chloride. The solutions are usually of equal concentration on the basis of the gram molecular weights per liter. But your accuracy is so poor that it is seldom the case that there is not an excess of one of the reactants. Sometimes it will be silver nitrate and sometimes it will be sodium chloride. Even though this is true, these reactions

are said to go to completion since one of the reactants, the one present in smaller concentration, disappears during the course of the reaction.

Equilibrium Reactions Many chemical reactions are equilibrium reactions. In a general equilibrium reaction



it is found that not only do A and B react to form C and D, but C and D react to form A and B. If a mixture of A and B is allowed to react, there will soon be some C and D formed, and they will begin to react. You will remember that the rates of chemical reactions were discussed in Chapter 5. It was pointed out that the speed of a chemical reaction increases with the concentration of the reactants. Therefore, in a mixture of A and B, the speed at which they react will be relatively great. But as the reaction proceeds and their concentrations diminish, they will react more and more slowly. On the other hand, the concentrations of C and D start at zero, and as the reaction proceeds, they increase. The rate at which C and D react will, therefore, increase as the reaction proceeds. Eventually the speed with which A and B react will equal the speed with which C and D react. This will be the *equilibrium point*. The concentrations of the four compounds, A, B, C, and D, will no longer change. A and B will continue to react to form C and D, but C and D will react just as rapidly to form A and B.

Most organic reactions are equilibrium reactions. They do not go to completion. The ionization of weak electrolytes is also an equilibrium reaction. This will be considered more fully in Chapter 15 under the discussion of pH .

NEW TERMS

Electrolyte, strong electrolyte, weak electrolyte, nonelectrolyte, electrolytic cell, anode, cathode, anion, cation, silver plate, galvanized iron, equilibrium point.

QUESTIONS

1. Give the assumptions of the Theory of Ionization and explain the experimental basis for these assumptions.

2. Give examples of three strong electrolytes, three weak electrolytes, and three nonelectrolytes. What is the difference between them in atomic structure?
3. Why is it now believed that strong electrolytes never exist as undissociated molecules? Does a positive ion have any attraction for a negative ion in a strong electrolyte?
4. Explain how hydrochloric acid conducts a current.
5. Why are cations attracted to the cathode in an electrolytic cell?
6. How is silver plate applied? Explain the electrode reactions.
7. As far as reaction of the metal with hot water and with weak acids in foods, what are the advantages and disadvantages of cooking utensils made of (a) iron, (b) copper, (c) aluminum, and (d) chromium?
8. Why would it be a mistake to try to cook a large amount of apple sauce in a galvanized bucket?
9. Why is it just as safe to store food in tin cans as in bowls?
10. Show the ions which are produced from the following substances: sodium sulfate, nitric acid, ammonium hydroxide, phosphoric acid, potassium bicarbonate, calcium chloride, acetic acid, sodium hydroxide. Indicate which are strongly and which are weakly ionized.
11. Write ionic reactions for the following: (a) copper sulfate + zinc, (b) zinc + hydrochloric acid, (c) sodium hydroxide + nitric acid, (d) silver nitrate + potassium chloride.

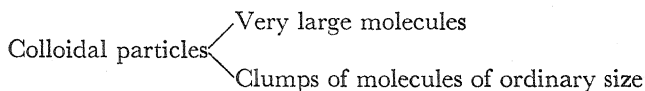
The Colloidal State

You have all had enough experience with mixtures to know that the size of the particles has a great influence on the way those mixtures behave. For one thing, the permanency of the mixture is very often influenced by the size of the particles. Take some sand which is quite coarse and shake it with water. Notice that the sand quickly separates from the water and settles to the bottom of the container. Then take some very finely divided sand and shake it with water. Notice how much longer it takes for the sand to separate.

Now sand and water do not form a colloidal dispersion. The particles are not small enough. But many other things in your environment are composed of colloidal dispersions. When one part of a mixture exists in the colloidal state, it is divided into tiny particles the size of very large molecules and is scattered uniformly through the other part of the mixture. In terms of actual dimensions, particles are called *colloidal* if *their diameter is between 1 and 100 millimicrons*. Since a micron is one thousandth of a millimeter, colloidal particles vary in diameter from 1 to 100 millionths of a millimeter. This is an approximate definition, since some colloidal particles may be a little larger or a little smaller than this size. Particles less than 1 millimicron in diameter are about the size of ordinary molecules, and when they are scattered through another substance, the mixture is a true solution. When particles are larger than 100 millimicrons in diameter, they tend to settle out, and they are called *sediments*. The sand particles are larger than 100 millimicrons.

Particles less than 100 millimicrons are not visible with microscopes, but above this diameter it is possible with a high-powered microscope to resolve them.

Colloidal-sized particles are either very large molecules, like protein or rubber molecules which have high molecular weights, or they are clumps of molecules of ordinary size.



Protein molecules vary considerably in molecular weight, but all are large. They vary from 15,000 to 70,000,000.

The colloidal particles are called the *dispersed phase*, or *micelles*, while the substance through which they are scattered is called the *dispersion medium*, or the *intermicellar medium*. When protein is dispersed in water, the protein is the dispersed phase and the water is the dispersion medium.

Types of Dispersions

You will remember that true solutions are catalogued into nine types, depending on the physical state of the solvent and the solute. There are, in the same manner, eight different types of colloidal dispersions. It is not possible to have a colloidal dispersion of a gas in a gas, since gaseous molecules are small and do not tend to cling together. A gas is made up of molecules moving independently of one another. When two gases are mixed, a true solution always results, since the molecules scatter through one another. But there are colloidal dispersions of gas in liquid, gas in solid, liquid in gas, etc. Some examples of each type of colloidal dispersion will be described.

Types of Colloidal Dispersions

- | | |
|---------------------|------------------------------------------------------|
| 1. Gas in liquid | Foams — beaten egg white, whipped cream, etc. |
| 2. Gas in solid | Cake, pumice, meerschaum, white hair, white flowers. |
| 3. Liquid in gas | Mist, fog. |
| 4. Liquid in liquid | Oil in vinegar, vinegar in oil, warm milk, gravy. |
| 5. Liquid in solid | Cheese, butter, opals, pearls. |
| 6. Solid in gas | Smoke, dust in air. |
| 7. Solid in liquid | Protein in water, starch paste, inks, gums in water. |
| 8. Solid in solid | Some colored glass, china, some gems. |

Remember that in each case the colloidal particle is so small that you cannot see it with a powerful microscope. If you can

see particles of dust in the air, or if you can see the water droplets in a fog, or the bubbles of gas in a cake, then you are observing particles which are very much larger than colloidal size. The colloidal dispersion will not necessarily be invisible to you, but the individual particles will. Cigarette smoke is an example of a colloidal dispersion of a solid in a gas. You can see the smoke, but you cannot see the individual particles of the smoke even under a powerful microscope.

The Difference Between a Solution and a Colloidal Dispersion

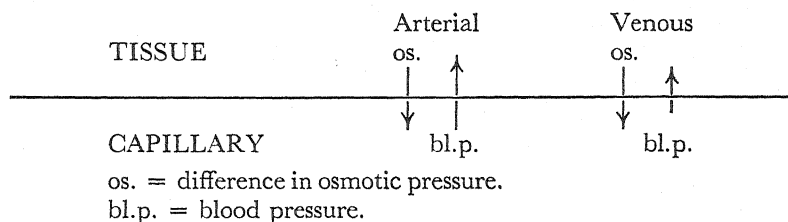
A solution and a colloidal dispersion have some properties in common. Both of them appear to be homogeneous. Actually a colloidal dispersion is not completely homogeneous, although it approaches this condition. Both will pass through a filter paper, since the pores in the paper are larger than colloidal particles.

There are, however, numerous semipermeable membranes with pores large enough to permit all solute and solvent molecules to pass through but with pores too small to permit the passage of colloidal particles. By dialysis a colloidal dispersion may be separated from a true solution. In, for example, a solution of sodium chloride and a dispersion of a protein in water, the sodium chloride will exist as ions of sodium and chloride in true solution, whereas the protein will exist as colloidal-sized particles. If this mixture is placed in a cellophane bag which has the proper pore size, and is suspended in water, the water molecules and the sodium and chloride ions can pass through the membrane, but the protein molecules cannot. If the bath in which the cellophane bag is suspended is arranged so that fresh water continually runs in and some of the bath water runs out, the sodium chloride will eventually be removed. In the cellophane bag there will eventually be a colloidal dispersion of protein in water with no sodium chloride present. The true solution of sodium chloride will have been separated from the colloidal dispersion of protein by *dialysis*.

True solutions have freezing points lower than the freezing point of the solvent, whereas colloidal dispersions have freezing points very close to that of the solvent. Likewise, the boiling point of a solution of a nonvolatile solute is higher than the boiling point of the solvent, while the boiling point of a colloidal

dispersion is the same or close to the boiling point of the dispersion medium.

Colloidal dispersions show some osmotic pressure, but it is much smaller than that of solutions. Occasionally in biological systems, the colloid osmotic pressure may be of importance. It has been shown, for example, that the colloid osmotic pressure of the blood is important in the return of intercellular fluid to the blood and, therefore, in the maintenance of blood volume. Blood is a complex mixture of many solutes dissolved in water (glucose, amino acids, nitrogen compounds, salts, etc.), the proteins, which are colloiddally dispersed, and the blood cells. Arterial blood is forced out into the capillaries of the tissues by the pumping action of the heart. The walls of the blood capillaries are permeable to solutions but not to colloidal dispersions. In the tissues, fluid is forced out between the cells. This is called the *intercellular fluid*. It has the same composition as the blood, except that it does not contain the colloiddally dispersed proteins or the blood cells. The osmotic pressure of the intercellular fluid is a little lower than that of the blood, since it depends on the concentration of the solutes, while that of the blood depends on the concentration of the same solutes PLUS the small additional osmotic pressure created by the proteins. If there were no flow of blood and no blood pressure from the pumping of the heart, water would tend to pass into the blood from the intercellular fluid. It would pass from a solution of low osmotic pressure to a solution of higher osmotic pressure. Now, on the arterial side, the blood pressure is sufficiently high so that it overcomes the osmotic pressure and forces fluid out of the blood stream. On the venous side, the blood pressure is lower, and the osmotic pressure permits the return of fluid to the blood stream.



On the arterial side, the blood pressure is greater than the difference in osmotic pressure between the blood and the inter-

cellular fluid (colloid osmotic pressure). Therefore, fluid passes out of the blood. On the venous side, the blood pressure is less than the difference in osmotic pressure. Therefore, fluid passes into the blood.

Tyndall Effect

The Tyndall effect is the reflection of light at right angles to a beam of light, which occurs when light is passed through a colloidal dispersion. You have all seen this effect when a shaft of light comes into a dark, dusty room. "The dust motes dance."

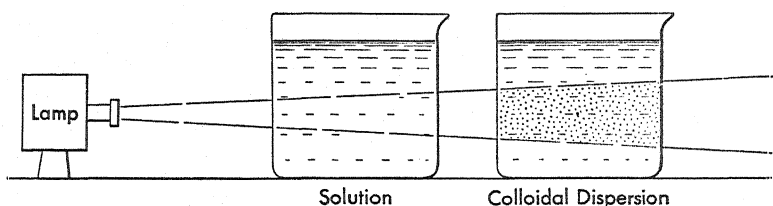


Fig. 14-1. *The Tyndall effect. When a beam of light is passed through a colloidal dispersion it is reflected out, but it is invisible as it passes through a true solution or a pure liquid.*

If the air is clean and there are no colloidal particles, the beam of light is invisible, if you are not in its path, until it falls on some object and is reflected back into your eyes. A true solution does not give the Tyndall effect, although most solutions in the laboratory have small amounts of dust colloiddally dispersed in them and will give a faint effect. This is a simple and rapid method for distinguishing true solutions and colloidal dispersions. The name "Tyndall" is for the scientist who first studied this phenomenon thoroughly, John Tyndall.

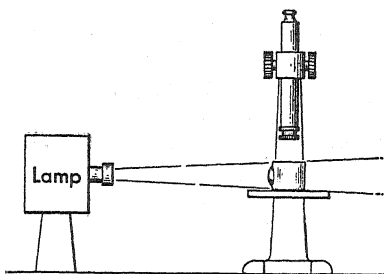
You have also seen the Tyndall effect when an airplane beacon sweeps through the sky. It is particularly noticeable on misty nights. Some of the colors which appear at sunset are the result of the Tyndall effect. When the sun is close enough to the horizon, so that you look at it through a thick layer of the earth's atmosphere, the colloiddally dispersed dust particles and droplets of water give the Tyndall effect.

It is possible to observe the light which is reflected in the Tyndall effect with a microscope. If the microscope is mounted in such a way that a beam of light can be directed across the

stage and through a colloidal dispersion, you will see tiny dots of light in continuous motion. You cannot see the colloidal particles, but you can see the light reflected from the particles. Ordinarily, under a microscope, a colloidal dispersion appears as a clear solution. But when a beam of light shines through the colloidal dispersion at right angles to the ocular of the microscope, each small particle reflects some light. A microscope set up in this fashion is called an *ultra-microscope*.

The tiny specks of light which we observe with an ultra-microscope move in zigzag paths. This is called Brownian movement. It is believed that the colloidal particles are in constant

Fig. 14-2. Ultramicroscope. A strong beam of light is directed across the stage of a microscope and through a colloidal dispersion. The reflection of light from each colloidal particle may be seen through the ocular.



random motion and that this motion is caused by the buffeting of the colloidal particles. The molecules of the dispersion medium are moving with kinetic motion, and they bump into the colloidal particles and knock them about in zigzag paths. This constant motion of colloidal particles undoubtedly accounts for the fact that they do not settle out.

Particle Charge

Most colloidal particles are charged and all the particles in a particular colloidal dispersion will possess the same charge. For example, when ferric hydroxide is colloiddally dispersed in water, each clump of ferric hydroxide molecules will have a positive charge, while colloidal gold in water has a negative charge. The charge is the result of (1) adsorption or inclusion of ions, (2) static electricity, or (3) ionization of the colloid particle.

When a substance is finely divided, it has an enormous surface area. When the surface area of one substance is extremely large, it frequently has the ability to attract other molecules to its surface and hold them there. This property is called adsorption.

Adsorption is the ability of a substance to hold another substance on its surface. If, for example, finely divided carbon (but much larger than colloidal size) is heated with a dye solution and then the mixture is filtered, much, if not all, of the dye will be removed from the solution. No chemical reaction has occurred. The



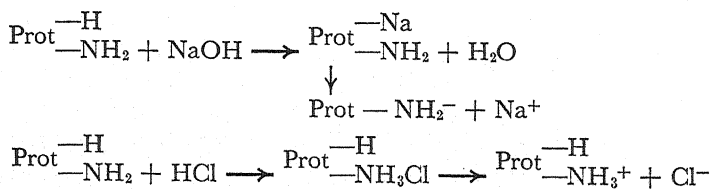
Fig. 14-3. Adsorption. Molecules are held on the surface of colloidal particles and other small particles.

charcoal has adsorbed the dye onto its surface. Notice that the word is *adsorption*. *Absorption* is the process by which a substance is taken up into and held within another substance.

It has already been pointed out that colloidal particles are very small — so small that they are invisible with an ordinary microscope. A small quantity of colloidal material will, therefore, possess a very large surface area. Adsorption by colloidal particles is a common phenomenon. If a colloidal dispersion is produced in the presence of ions, the colloidal particles may adsorb onto their surface one type of ion. For example, ferric hydroxide clumps will either adsorb or enclose hydrogen ions or ferric ions and the colloidal particle will then be positively charged.

Static electricity is the charge which develops on objects when electrons are removed or added to it. For example, if a hard rubber comb is run vigorously through your hair in a dry atmosphere, a charge will develop on the comb and the opposite charge on your hair. Your hair will stand out, as each hair with the same charge repels every other hair. In the same way, a few electrons may be removed from a colloidal particle to give it a positive charge, or a few may be added to a colloidal particle to give it a negative charge.

A few colloids which are very large molecules are capable of ionizing. This is especially true of the proteins. Proteins are amphoteric substances, reacting like a base in the presence of an acid and like an acid in the presence of a base.



In the presence of a base, the protein forms a salt. This ionizes to give a negative protein ion and a positive metal ion. In the presence of an acid, the protein acts as a derivative of ammonia, NH_3 , and forms a salt corresponding to ammonium chloride, NH_4Cl . This salt ionizes to form a positive protein ion and a negative nonmetal or radical ion.

The charge on the colloidal particles is another factor which contributes to their stability. Since, in a given colloidal dispersion, all the colloidal particles have the same charge, they repel one another and there is no tendency to come together and form larger particles which will settle out.

Precipitation

Colloidal dispersions may be precipitated by the addition of an electrolyte to the colloidal dispersion or by passing the dispersion through charged plates. If a salt, such as sodium chloride, is added to a colloidal dispersion, the dispersed phase will settle out. The electric charge on the colloidal particles seems to account for this change in the presence of electrolytes. However, it is no simple neutralization of the charge. Colloidal particles which are positively charged are more efficiently precipitated by a salt which has a trivalent negative ion, such as sodium phosphate, Na_3PO_4 . A divalent negative ion, such as, for example, sulfate, SO_4^{--} , is more effective than a monovalent ion like chloride, Cl^- . For negatively charged colloidal particles, it is the positive ion of the electrolyte which is most important. Here,

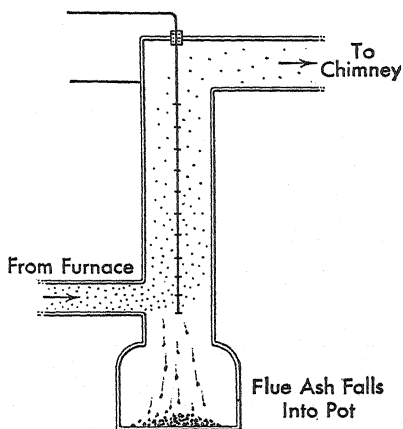


Fig. 14-4. Cottrell precipitator. Flue gases are passed through a stack where the walls are lined with metal plates with one charge and a wire has the other charge. The colloidal particles of smoke are discharged and precipitate into the pot.

too, the trivalent ion is more efficient than a divalent or monovalent ion: $\text{Al}^{+++} > \text{Ca}^{++} > \text{K}^+$, for example.

There are many examples of the precipitation of colloidal dispersions by the action of electrolytes. The deltas which form at the mouths of rivers are caused by the precipitation of colloiddally dispersed clay when the river water comes in contact with the salty sea water. Soap is precipitated from a dispersion by the addition of large amounts of salt during its manufacture and purification. Salts are added to dye baths (dyes are usually colloidal-sized particles) to hasten the precipitation of the dye and to make it take evenly.

Smokes and dusts from factories are often precipitated by the Cottrell process. The smoke passes up a chimney in which is suspended a charged wire. Plates with the opposite charge line the sides of the chimney. When the colloiddally dispersed and charged smoke particles come in contact with the plates or wire, they are precipitated and fall to the bottom of the flue. The amount of "fly ash" and soot given off a smoke stack can be materially decreased by this precipitation.

Colloidal dispersions and true solutions differ in the following respects:

	<i>Colloidal dispersion</i>	<i>True solution</i>
Particle size	1-100 m μ .	1 m μ
Appearance	Clear or opalescent	Clear
Filtration	Passes through filter paper	Passes through filter paper
Dialysis	Does not pass through semipermeable membrane	Passes through
Freezing point	Approximately equal to dispersion medium	Lower than solvent
Boiling point	Approximately equal to dispersion medium	Higher than solvent
Osmotic pressure	Small	Shows greater osmotic pressure
Tyndall effect	Yes	No
Precipitation by electrolytes	Yes	No

Preparation of Colloidal Dispersions

Colloidal dispersions may be prepared either by starting with very small particles and condensing them to colloidal size or by

starting with large particles and breaking them down to colloidal size.

A. Condensation methods.

1. Chemical method. When a difficultly soluble substance is produced by a chemical reaction in a solution, it usually precipitates. But if the concentration of the reactants is low, or if the temperature is low, it may form colloidal-sized particles. Some of you have had difficulty in filtering barium sulfate when it is precipitated at room temperature, because it runs through the filter paper. The barium sulfate has formed a colloidal dispersion. The colloidal dispersion of ferric hydroxide is another example.

2. Replacement of solvent. If a substance is dissolved and the solvent is quickly changed to one in which the material is not very soluble, it will frequently form a colloidal dispersion. For example, if sulfur is dissolved in alcohol and then the solution is added to water, a colloidal dispersion of sulfur in water will form. The sulfur is almost insoluble in water and when the solvent is quickly changed from alcohol to water, the sulfur forms clumps of colloidal size.

B. Dispersion methods.

1. Peptization. When some substances come in contact with another in which they are not soluble, colloidal-sized particles break off and become dispersed through the medium. This is *peptization*. It is observed when soap and water come in contact. They automatically form a colloidal dispersion of soap in water.

2. Mechanical. There are a number of mechanical devices for preparing colloidal-sized particles. There are colloid mills, which will grind solids to colloidal size. Paint pigments are usually ground in colloid mills. A homogenizer for the preparation of homogenized milk is a mechanical device for producing cream droplets of approximately colloidal size in the milk. The milk is passed through a nozzle which has extremely fine holes in it, and the large cream droplets are broken up into smaller ones.

Hydrophobic and Hydrophilic Colloidal Dispersions

Colloidal dispersions in which the dispersion medium is water are either *hydrophobic* or *hydrophilic*. Since most of the colloidal

dispersions which you encounter are water dispersions, it is worth while to differentiate these two types of dispersions. Literally, the word "hydrophobic" means "water hating," and the word "hydrophilic" means "water loving." But these literal definitions do not tell much about the colloidal dispersions and their properties.

A hydrophilic colloidal dispersion is one in which there is attraction between the colloidal particles and the dispersion medium. If the dispersion medium is some substance other than water, the colloidal dispersion is called *lyophilic*. *A hydrophobic colloidal dispersion is one in which there is no attraction between the colloidal particles and the dispersion medium.* The dispersion is called *lyophobic* if the dispersion medium is some substance other than water. Hydrophobic colloidal dispersions are dispersions of substances which are elements like gold, salts like arsenic trisulfide, oxides, and hydroxides. Hydrophilic colloidal dispersions are dispersions of proteins, starches, gums, and soaps. They differ in the following respects:

1. A hydrophobic colloidal dispersion is readily precipitated by small amounts of electrolytes, while a hydrophilic colloidal dispersion requires rather large amounts of electrolyte.
2. The precipitation of a hydrophobic colloidal dispersion is usually irreversible, while a hydrophilic is reversible.
3. The electric charge on a hydrophobic colloid is always the same. On a hydrophilic, it sometimes changes with the acidity or basicity of the dispersion medium.
4. The viscosity of a hydrophobic colloid is the same as the viscosity of water. That of a hydrophilic colloid rises with decreasing temperature. If you chill a colloidal dispersion of gold in water, the viscosity will show practically no change, but if you chill a colloidal dispersion of starch in water, it will thicken.

Emulsions An emulsion is a colloidal dispersion of a liquid in a liquid. The liquids must be difficultly soluble in one another, so that a true solution does not result. The size of the dispersed droplets in an emulsion is usually in the upper range of colloidal dimensions. When you shake oil and vinegar, or kerosene and water, you prepare an emulsion by mechanical means. Such an emulsion is very unstable. The droplets rapidly coalesce to form droplets visible to the eye, and soon two layers form. If an

emulsifying agent is present, the two liquids form an emulsion more rapidly and the emulsion is permanent, or at least the permanency is increased. When water is one of the liquids which form the emulsion, the emulsifying agent is usually a hydrophilic colloid, such as gums, proteins, or starches. The emulsifying agent appears to hasten the emulsification and stabilize the emulsion by coating the droplets and preventing their coalescence. Some emulsifying agents change the surface tension of one of the liquids and have the effect then of diminishing the coalescence of the droplets. *An emulsifying agent is a substance which promotes and stabilizes emulsions.* Occasionally, a finely powdered substance will act as an emulsifying agent. Finely ground paprika has a stabilizing effect on French dressing.

There are many examples of emulsions and of emulsifying agents in cookery. Gravies, sauces, cream soups, mayonnaise, and batters are all examples of oil and water emulsions. In mayonnaise, the emulsion is water in oil, but the others are emulsions of oil in water. In all these, protein of egg and flour, the starch of flour, and cornstarch act as emulsifying agents.

In the digestive tract there is an excellent example of a very efficient emulsifying agent. The bile salts, which are present in bile, act as an emulsifying agent. Food fat is liquid by the time it enters the duodenum. The mobility of the intestine mixes the fat with the fluid of the digestive juices and that which was taken with the food. This emulsion is promoted and stabilized by the presence of bile salts. If the bile salts are absent, as they are during obstruction of the bile duct, the digestion of fat is seriously impaired.

Gels A gel is the semisolid mixture which is produced when a hydrophilic colloidal dispersion is cooled. When starches, many proteins, gums, and pectins are dispersed in water in sufficient concentration and then are cooled, they set to a gel. As cooling takes place, the colloidal particles adsorb water molecules on their surface and grow in size. These particles make either a brush pile or a honeycomb network and trap the rest of the water in the cells which they form. A brush pile arrangement is a random arrangement of hydrated fibers or filaments. A honeycomb arrangement is an arrangement similar to that found in the honeycomb, an ordered arrangement. Some scientists

who have studied gels believe that certain substances tend to form brush pile gels, while others form the honeycomb type.

When a gel is turned out on a plate and allowed to stand for a time, some of the water held in the cells oozes out. This is

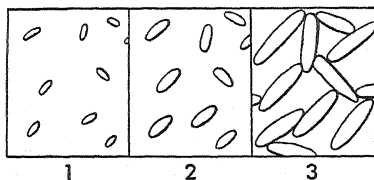


Fig. 14-5. Gel formation. As the temperature of a hydrophilic colloidal dispersion falls, water is adsorbed on the walls of the particles (2) until finally they form a brush pile or honeycomb and trap the remaining water in the interstices. This last stage, a semi-solid, is called a gel.

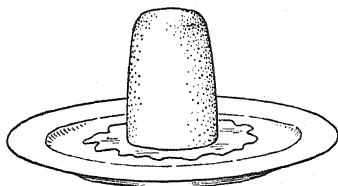


Fig. 14-6. Syneresis or "weeping" of a gel. When a fruit jelly is turned out on a plate and allowed to stand, juice slowly seeps out and forms a small pool.

syneresis, the loss of fluid by a gel on standing. A cook says that the gel "weeps." The tendency of gels to synerese varies with the hydrophilic colloid. Some show no tendency to shrink and lose fluid. Others, like cranberry jelly, show a very marked tendency to synerese.

Fruit jellies are examples of gels of pectin and water. They are complex systems and the success of the gel depends not only on the pectin, but also on the acidity of the solution and the amount of sugar used. Gelatin mixtures are typical gels in which gelatin, a protein, is the hydrophilic colloid. Egg custards are also gels in which the protein of the egg is the hydrophilic colloid.

Cutting or whipping a gel destroys the cells which the hydrophilic colloid has formed, and the gel turns to a thick syrup. Many of you have had the experience of cutting into a fruit jelly in a glass a number of times and having it lose its gelation. Or some of you have whipped grape jelly with a fork when you wished to use it as a grape flavor.

A blood clot forms a typical gel. When blood is shed, a chemical reaction takes place which results in the production of a new protein, fibrin. The fibrin forms a gel with the water of the blood and holds the blood cells and the fluid of the blood in the inter-

stices of the gel. If a freshly gelled blood clot is cut with a knife or beaten with a fork, the fluid of the blood containing colloiddally dispersed proteins and solutes will run out and will carry with it some of the blood cells. If the clot is allowed to stand, it will synerese. Only the fluid of the blood will escape from the gel and take with it the colloiddally dispersed proteins and the substances dissolved in the water of the blood. This is the serum which you see ooze out of a clot on a wound. As it dries, it leaves a clear amber residue around and over the clot.

Foams A foam is a colloiddal dispersion of a gas in a liquid. Those which are permanent or which have appreciable stability contain a *protective colloid*. A protective colloid is *any colloid which stabilizes another colloiddal dispersion*. Protective colloids not only stabilize foams, but they are important in all types of colloiddal dispersions. An emulsifying agent is a type of protective colloid. When one of the substances which make up the colloiddal dispersion is water, hydrophilic colloids act as protective colloids. The importance of these agents can readily be demonstrated by attempting to prepare a foam by beating water with an egg beater. No foam results. But if egg albumin is present in sufficient concentration, as it is in egg white, the foam is readily produced and is fairly stable. The lather on soap is a foam of air in water with the soap as protective colloid.

NEW TERMS

Colloiddal dispersion, sediments, dispersed phase or micelles, dispersion medium or intermicellar medium, intercellular fluid, Tyndall effect, adsorption, peptization, hydrophobic, hydrophilic, emulsion, emulsifying agent, gel, syneresis, protective colloid.

QUESTIONS

1. Give an example of each type of colloiddal dispersion. What one test will show the difference between true solutions and colloiddal dispersions?
2. List all the differences between true solutions and colloiddal dispersions.
3. How can the production of colloiddal dispersions be avoided? How can it be achieved?

4. Explain why some substances, such as proteins, do not form true solutions, but form colloidal dispersions.
5. Suppose that you have some water in which sodium chloride is dissolved and egg albumin is colloiddally dispersed. How may they be separated?
6. What is "colloid osmotic pressure"? Why is it usually low? What is its significance in the circulation of the blood?
7. How may colloidal particles be precipitated?
8. Clay particles are negatively charged. Which salt will be more effective in precipitating them — Na_2SO_4 , CaCl_2 , or AlCl_3 ? If they were positively charged, what salts would be most effective?
9. How can we account for the fact that colloid particles carry charges?
10. What is the difference between a hydrophobic colloid and a hydrophilic colloid? Give examples of each.
11. What is an emulsion? Why is a protective colloid effective in stabilizing an emulsion? Give an example of an emulsion and a substance which will act as an emulsifying agent for it.
12. Corn oil and vinegar form a very impermanent emulsion when they are shaken together. Give three methods for stabilizing the emulsion and explain why each is effective.
13. What is a gel? Give three examples of gels. What is the structure of the gel?
14. On standing meat gravy thickens to a starch gel. If this is stored in the refrigerator for several days, it becomes covered with cracks and a thin brown liquid oozes out. Explain.
15. Give three examples of foams and explain the action of the protective colloid in each case.

Quantitative Solutions

The concentrations of solutes in solution may be expressed in a number of different ways: *percentage* by weight or volume, *molarity*, or *normality*. These methods give an accurate measure of the amount of solute in a given solution. In very dilute solutions of acids and bases, *pH* is usually used. This method does not give the quantity of solute, but the quantities of hydrogen and hydroxyl ions which are present.

MEASURES OF CONCENTRATION

Percentage

The concentration of many solutions is expressed in terms of percentage by weight of the solute in the solution. A 5% salt solution is one in which 5 grams of sodium chloride is dissolved in 100 grams of solution; or, since the 5 grams of sodium chloride make up part of the 100 grams, it is a solution in which 5 grams of sodium chloride is dissolved in 95 grams of solvent. It is simple to calculate the percentage of a solution by dividing the weight of the solute by the sum of the weights of the solute and the solvent, and multiplying by 100.

$$\text{Percentage by weight} = \frac{\text{Wt. of solute}}{\text{Wt. of solute} + \text{solvent}} \times 100$$

Occasionally, when the solution is made up of a liquid dissolved in another liquid, the percentage will be expressed in terms of volumes. It is always designated "per cent by volume" or "volume per cent." Thus, a solution which contains 5% by volume of alcohol has 5 milliliters of alcohol for each 100 milliliters of solution. Since the volume of a solution of a liquid in a liquid is not exactly equal to the sum of the volumes of the two liquids, but is sometimes slightly smaller and sometimes slightly

larger, this method of designating a solution is difficult to use accurately. Often a solution by volume is made approximately. For example, a 5% by volume solution of alcohol and water may be made by dissolving 5 parts of alcohol in 95 parts of water, but this solution will be slightly less than 5% by volume.

$$\text{Percentage by volume} = \frac{\text{Vol. of solute}}{\text{Vol. of solution}} \times 100$$

Molarity

A molar solution expresses the number of gram molecular weights of solute in 1 liter of solution. Thus a 1 molar solution contains 1 gram molecular weight of solute per liter of solution, while a 5 molar solution contains 5 gram molecular weights of solute per liter of solution, and a 0.1 molar solution contains 0.1 gram molecular weight per liter of solution. Notice that these solutions are defined on the basis of gram molecular weights *per liter of solution*, while the *molal* solutions which you used in calculating freezing and boiling points were defined on the basis of the number of gram molecular weights per 1000 grams of water. One liter of an aqueous solution seldom has 1000 grams of water. The number of gram molecular weights per liter of solution is called the *molarity* of the solution.

Since the gram molecular weight of sulfuric acid is 98 (2 + 32 + 64), 1 molar sulfuric acid contains 98 grams of H_2SO_4 per liter of solution, 5 molar sulfuric acid contains 490 grams of H_2SO_4 per liter of solution, and 0.1 molar sulfuric acid contains 9.8 grams of H_2SO_4 per liter of solution.

A capital *M* is used to stand for "molar," and the number precedes it unless it is 1 molar, when no number is used.

$M \text{ H}_2\text{SO}_4$ means a 1 molar solution of sulfuric acid.

$5M \text{ H}_2\text{SO}_4$ means a 5 molar solution of sulfuric acid.

$0.1M \text{ H}_2\text{SO}_4$ or $M/10 \text{ H}_2\text{SO}_4$ means a 0.1 molar solution of sulfuric acid.

You will remember that the word "mole" is a synonym for the term "gram molecular weight." Thus a 5 molar solution contains 5 "moles" of solute per liter of solution, in other words, 5 "gram molecular weights" of solute per liter.

In order to calculate the molarity of a solution, divide the number of grams dissolved in 1 liter of solution by its gram

molecular weight. This will give you the number of gram molecular weights or the number of moles in a liter of solution.

$$\text{Molarity} = \frac{\text{Grams solute in 1 liter of solution}}{\text{Gram molecular weight of solute}}$$

PROBLEM: What is the molarity of a solution which contains 4.9 grams of sulfuric acid dissolved in 1 liter of solution?

ANSWER: The gram molecular weight of H_2SO_4 is 98 grams.

$$\frac{4.9 \text{ g.}}{98 \text{ g.}} = 0.05M \text{ H}_2\text{SO}_4$$

Molarity is used in expressing the concentration of solutions, no matter what the volume. You may have 5 ml. of a $0.1M \text{ H}_2\text{SO}_4$, or you may have 100 liters. The proportion of solute to solvent is the same, no matter what the volume. But the concentration is always referred back to the quantity of solute which would be dissolved if you did have 1 liter.

PROBLEM: How much sulfuric acid is dissolved in 5 ml. of $0.1M \text{ H}_2\text{SO}_4$?

ANSWER: The gram molecular weight of H_2SO_4 is 98. Therefore, $0.1M \text{ H}_2\text{SO}_4$ contains 9.8 grams of sulfuric acid per liter of solution.

$$98 \times 0.1M = 9.8 \text{ g./l.}$$

To find the amount in 5 milliliters of solution, divide by 1000, the number of milliliters in 1 liter, and multiply by 5.

$$9.8 \text{ g. per liter} \times \frac{5 \text{ ml.}}{1000 \text{ ml.}} = 0.049 \text{ g. in 5 ml.}$$

PROBLEM: What is the molarity of a solution which contains 20 grams of sodium hydroxide in 100 milliliters of solution?

ANSWER: First calculate the number of grams of NaOH in 1 liter or 1000 milliliters of solution.

$$20 \text{ g.} \times \frac{1000 \text{ ml.}}{100 \text{ ml.}} = 200 \text{ g. NaOH per liter}$$

Then calculate the molarity by dividing the number of grams per liter by the gram molecular weight. The gram molecular weight of NaOH is 40 (23 + 16 + 1).

$$\frac{200 \text{ g. per liter}}{40 \text{ g.}} = 5M \text{ NaOH}$$

When a quantitative solution is made up to 1 liter or to any other definite volume, the solute is dissolved in a small amount of the solvent in a calibrated flask. More solvent is carefully added until the volume is exactly up to the mark on the flask. Flasks which are commonly used for precise work have long, slender necks, so that the addition of a small amount of solvent causes a marked rise of the solution in the neck of the flask. These are called volumetric flasks. They are calibrated to contain a specific volume at a definite temperature, usually 20°C . If there is either a marked evolution of heat or a loss of heat when the solute dissolves (positive or negative heat of solution) the temperature must be brought to 20°C . before the solution is made up to the mark.

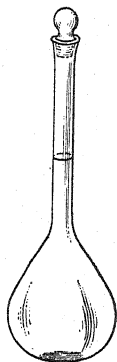


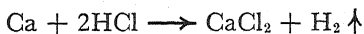
Fig. 15-1. Volumetric flask for making quantitative solutions. The mark on the long neck of the flask is calibrated so that when the liquid is adjusted to this mark, the flask will contain at 20°C ., exactly the quantity designated.

Normality

A normal solution expresses the number of gram equivalent weights per liter of solution. A one normal solution contains one gram equivalent weight of solute per liter of solution, while a five normal solution contains five gram equivalent weights, etc. The number of gram equivalent weights of solute in 1 liter of solution is called the *normality*. This is written with a capital *N* as $N\text{ HCl}$ or $5N\text{ H}_2\text{SO}_4$ or $0.1N\text{ NaOH}$. Normal solutions have distinct advantages over molar solutions since equal volumes of solutions of the same normality react exactly with one another. They are, therefore, much more widely used in quantitative chemistry than molar solutions. This will be fully discussed later.

A gram equivalent weight (see p. 67) is the weight of an element which is chemically equivalent to 1.008 grams of hydrogen. "Chemically equivalent" means that this quantity of an element will act in the place of, or similarly to, 1.008 grams of

hydrogen. You probably recognize that this quantity of hydrogen is one gram atomic weight and contains 6.02×10^{23} atoms of hydrogen (Avogadro's number). An element like sodium has the same valence as hydrogen and undergoes some similar reactions. Therefore, it will take the same number of sodium atoms, 6.02×10^{23} , to take the place of the hydrogen. This is the number of atoms in one gram atomic weight of sodium. An element like chlorine will react with hydrogen in the ratio of one atom for one atom. Therefore, the gram equivalent weight of chlorine is the weight which contains 6.02×10^{23} atoms, or one gram atomic weight. On the other hand, an element like calcium reacts as if it were equivalent to two hydrogen atoms. In the following typical reaction, one atom of calcium replaces two atoms of hydrogen:



Therefore, the weight of calcium which is chemically equivalent to 1.008 grams of hydrogen is one-half a gram atomic weight.

Gram equivalent weight of Na = gram atomic weight

Gram equivalent weight of Cl = gram atomic weight

Gram equivalent weight of Ca = gram atomic weight \div 2

In other words, the gram equivalent weight of an element is equal to its atomic weight divided by its valence.

$$\text{Gram equivalent weight} = \frac{\text{Gram atomic weight}}{\text{Valence}}$$

The gram equivalent weight of a compound is the weight of the compound which contains 1.008 grams of potential hydrogen ion or its chemical equivalent. Let us look at acids first, since they contain hydrogen ions. What weight of an acid contains 1.008 grams of potential ion? If the gram molecular weights of acids such as HCl, HNO₃, and HBr are calculated, it is recognized that this gram molecular weight of acid contains exactly 1.008 grams of hydrogen ion. With acids like H₂S, H₂CO₃, or H₂SO₄, a gram molecular weight contains 2.016 grams of potential hydrogen ion. Therefore, the gram equivalent weight of these acids is equal to half the gram molecular weight. An acid such as H₃PO₄ contains in one gram molecular weight 3.024 grams of potential hydrogen ion. Therefore, the gram equivalent weight is equal to one-third the gram molecular weight. Notice

that the gram equivalent weight is defined on the basis of "potential hydrogen ion." In an acid like acetic, $\text{HC}_2\text{H}_3\text{O}_2$, only one of the hydrogens has the ability to ionize. Since acetic acid is a weak acid, most of this hydrogen does not exist at one moment as hydrogen ion, but since it is capable of ionizing, it is counted. One gram molecular weight of $\text{HC}_2\text{H}_3\text{O}_2$ has just 1.008 grams of potential hydrogen ion and the gram equivalent weight is equal to the gram molecular weight.

Gram equivalent weight of HCl = gram molecular weight

Gram equivalent weight of H_2SO_4 = gram molecular weight \div 2

Gram equivalent weight of H_3PO_4 = gram molecular weight \div 3

The gram equivalent weight of compounds which do not contain hydrogen ions is the weight which contains the chemical equivalent of 1.008 grams of hydrogen ions. Since one sodium ion is equivalent to one hydrogen ion, salts which contain one sodium ion in each molecule, such as NaNO_3 , NaCl , and NaNO_2 , possess the equivalent of 1.008 grams of hydrogen ion in one gram molecular weight. In other words, the gram equivalent weight of a salt like NaNO_3 is equal to the gram molecular weight. Salts which contain calcium possess an element which reacts in such a way that one calcium ion takes the place of *two* hydrogen ions. One gram molecular weight of salts such as CaCl_2 , CaCO_3 , and CaSO_4 contains the chemical equivalent of 2.016 grams of hydrogen ion. The gram equivalent weight of a salt such as CaCl_2 is equal to one-half the gram molecular weight. An ion like aluminum which has a valence of plus three takes the place of three hydrogen ions, and in salts like AlCl_3 or FeCl_3 the gram equivalent weight is equal to one-third the gram molecular weight. In salts like ferric sulfate, $\text{Fe}_2(\text{SO}_4)_3$, there are two ferric ions in one gram molecular weight of the salt, and each ferric ion is chemically equivalent to three hydrogen ions. This means that one gram molecular weight of the salt has *six* times the chemical equivalent of 1.008 grams of hydrogen ion. The gram equivalent weight of $\text{Fe}_2(\text{SO}_4)_3$ is one-sixth its gram molecular weight.

GEW of NaCl = GMW

GEW of CaCl_2 = GMW \div 2

GEW of AlCl_3 = GMW \div 3

GEW of $\text{Fe}_2(\text{SO}_4)_3$ = GMW \div 6

Occasionally you will encounter a mixed salt or an acid salt in which there are two positive ions. Both of these are considered in calculating the gram equivalent weight. NaHCO_3 , sodium bicarbonate, has one potential hydrogen ion and the equivalent of one hydrogen ion in the sodium ion. The gram equivalent weight of NaHCO_3 is, therefore, one-half its gram molecular weight.

Hydroxides can be calculated in a manner similar to that used for salts, or you can use the hydroxide ions as a basis for the calculation. Since one hydroxide ion reacts with one hydrogen ion, it is chemically equivalent to it. One gram molecular weight of sodium hydroxide, NaOH , contains the chemical equivalent of 1.008 grams of hydrogen ion, while a gram molecular weight of calcium hydroxide, Ca(OH)_2 , contains the chemical equivalent of 2.016 grams of hydrogen ion. The gram equivalent weight of sodium hydroxide is equal to its gram molecular weight and the gram equivalent weight of calcium hydroxide is one-half its gram molecular weight.

The Gram Equivalent Weight

Examples of acids

$$\text{HCl} \quad \text{GEW} = \text{GMW} = 36.465 \text{ grams}$$

$$\text{H}_2\text{SO}_4 \quad \text{GEW} = \frac{\text{GMW}}{2} = 49.038 \text{ grams}$$

$$\text{H}_3\text{PO}_4 \quad \text{GEW} = \frac{\text{GMW}}{3} = 32.668 \text{ grams}$$

Examples of salts

$$\text{NaCl} \quad \text{GEW} = \text{GMW} = 58.454 \text{ grams}$$

$$\text{K}_2\text{SO}_4 \quad \text{GEW} = \frac{\text{GMW}}{2} = 87.126 \text{ grams}$$

$$\text{Ca(NO}_3)_2 \quad \text{GEW} = \frac{\text{GMW}}{2} = 92.048 \text{ grams}$$

$$\text{Al}_2(\text{SO}_4)_3 \quad \text{GEW} = \frac{\text{GMW}}{6} = 57.02 \text{ grams}$$

Examples of hydroxides

$$\text{NaOH} \quad \text{GEW} = \text{GMW} = 40.005 \text{ grams}$$

$$\text{Mg(OH)}_2 \quad \text{GEW} = \frac{\text{GMW}}{2} = 29.168 \text{ grams}$$

$$\text{Al(OH)}_3 \quad \text{GEW} = \frac{\text{GMW}}{3} = 25.998 \text{ grams}$$

In order to calculate the number of grams of solute in 1 liter of a solution where the concentration is expressed in normality, multiply the gram equivalent weight of the solute by the normality.

$$\text{GEW} \times N = \text{Number of grams solute per liter of solution}$$

PROBLEM: How many grams of sodium hydroxide must be dissolved to make 1 liter of 5*N* NaOH?

ANSWER: The gram equivalent weight of NaOH is equal to the gram molecular weight and this is 40.005 grams. There will be five gram equivalent weights in each liter of solution.

$$40.005 \times 5 = 200.025 \text{ g. of NaOH per liter of solution}$$

PROBLEM: Calculate the number of grams of solute in 5 milliliters of 0.1*N* H₂SO₄.

ANSWER: The gram equivalent weight of H₂SO₄ is one-half the gram molecular weight or $98 \div 2 = 49$ grams. First calculate the number of grams of solute in 1 liter of solution by multiplying the gram equivalent weight by the normality.

$$49 \text{ g.} \times 0.1N = 4.9 \text{ g. per liter}$$

Divide the number of grams of solute in 1 liter by 1000, the number of milliliters in a liter, and multiply by the number of milliliters in the sample.

$$4.9 \times 5 \text{ ml.} / 1000 \text{ ml.} = 0.0245 \text{ g. H}_2\text{SO}_4 \text{ in 5 ml.}$$

These two steps may be carried out at the same time. The calculations then become:

$$49 \times 0.1N \times 5 \text{ ml.} / 1000 \text{ ml.} = 0.0245 \text{ g. H}_2\text{SO}_4 \text{ in 5 ml.}$$

PROBLEM: One hundred milliliters of a solution contains 15 grams of Ca(NO₃)₂. What is the normality of the solution?

ANSWER: The gram equivalent weight of Ca(NO₃)₂ is equal to one-half the gram molecular weight. $\text{GEW} = 164 \div 2 = 82 \text{ g.}$ A solution which contains 15 grams of solute in 100 milliliters will contain 1000/100 in 1000 milliliters or 1 liter.

$$15 \times 1000 \text{ ml.} / 100 \text{ ml.} = 150 \text{ g. Ca(NO}_3)_2 \text{ in 1 l.}$$

To calculate the normality of the solution, the number of grams of the solute in 1 liter is divided by its gram equivalent weight:

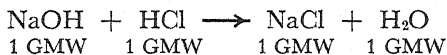
$$150 \text{ g.} / 82 \text{ g.} = 1.95N \text{ Ca(NO}_3)_2$$

Both steps may be combined:

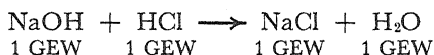
$$\frac{15 \text{ g.} \times 1000 \text{ ml./100 ml.}}{82 \text{ g.}} = 1.95N \text{ Ca(NO}_3)_2$$

Reactions between Solutions When solutions react, a one normal solution will react with an equal volume of another one normal solution. It can readily be understood why this is true if the reactions of some solutions of acids and bases are considered.

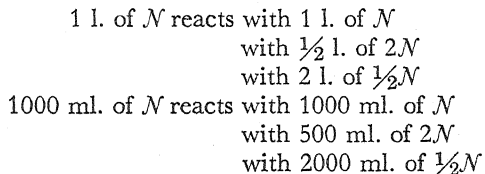
For example, in the reaction of sodium hydroxide and hydrochloric acid, the balanced equation shows that one gram molecular weight of sodium hydroxide exactly reacts with one gram molecular weight of hydrochloric acid to produce one gram molecular weight of sodium chloride and one gram molecular weight of water.



For each of these four compounds, sodium hydroxide, hydrochloric acid, sodium chloride, and water, the gram equivalent weight is equal to the gram molecular weight. Therefore:



In terms of volumes of quantitative solutions, one gram equivalent weight is dissolved in 1 liter of one normal solution, or 500 milliliters of 2 normal solution, or 2 liters of 0.5 normal solution, etc. In other words, when it is said that one gram equivalent weight of sodium hydroxide will react with one gram equivalent weight of hydrochloric acid, it is implied that 1 liter of N NaOH will react with 1 liter of N HCl, or 500 ml. of $2N$ HCl, or 2 liters of $\frac{1}{2}N$ HCl. If all volumes are expressed in the same units:



The same relationships hold, no matter what the number of gram equivalent weights which react, and no matter what the

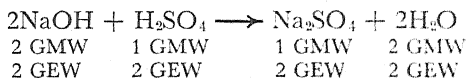
volume or normality of the solution. The volume of one solution multiplied by its normality is equal to the volume of the other solution multiplied by its normality.

$$\text{Vol. A} \times N \text{ of A} = \text{Vol. B} \times N \text{ of B}$$

You may wonder if this relationship actually applies to all solutions, since the example used, the reaction of sodium hydroxide and hydrochloric acid, is simple. The same relationship holds where the ratio of the reacting molecules is not one for one. Consider the reaction of sodium hydroxide and sulfuric acid:



The balanced equation shows that two molecules of sodium hydroxide react for every molecule of sulfuric acid. It also shows that two gram molecular weights of sodium hydroxide react with one gram molecular weight of sulfuric acid.



Since the gram equivalent weight of sodium hydroxide is equal to the gram molecular weight, two gram molecular weights will be equal to two gram equivalent weights. With sulfuric acid, however, the gram equivalent weight is equal to one-half the gram molecular weight, so one gram molecular weight will be equal to two gram equivalent weights.

In this reaction, as in the first example, the *same number of gram equivalent weights of each substance react*. This is true of all reactions. Since the volume of a solution expressed in liters multiplied by the normality gives the number of gram equivalent weights present,

$$\text{Vol. (liters)} \times N = \text{No. of GEW}$$

the equation of volume and normality will apply to all solutions.

$$\text{Vol. A} \times N \text{ of A} = \text{Vol. B} \times N \text{ of B}$$

It will be valid if the volumes on each side are expressed in liters or if the volumes on each side are expressed in thousandths

of a liter or milliliters. But the *volumes* on each side of the equation *must be expressed in the same units*.

Actually, in proving that when solutions react chemically the product of their volumes and normalities are exactly equal, the cart has come before the horse. The concept of normality was developed so that this simple relationship would hold true. This is the advantage of normality over molarity. The relationship *does not hold for molar solutions*.

Determining Normality The normality of a solution may be determined in the laboratory by the use of the relationship between normality and volume. The procedure is called a *titration*. To determine the concentration of a solution, a solution of a compound, with a known concentration, with which it will react is prepared. This is the *standard solution*. A standard solution is a solution of known concentration. The titration is carried out by measuring accurately the volume of the standard solution which will exactly react with a given volume of the solution of unknown concentration. For example, hydrochloric acid will react with a base such as sodium hydroxide. A standard solution of sodium hydroxide might be made up which is exactly 1.5 normal. By titration it could be determined that 10 milliliters of sodium hydroxide exactly react with, or neutralize, 15 milliliters of hydrochloric acid. The normality of the hydrochloric acid could then be calculated.

$$\begin{aligned}\text{Vol.} \times N \text{ NaOH} &= \text{Vol.} \times N \text{ HCl} \\ 10 \text{ ml.} \times 1.5N &= 15 \text{ ml.} \times X \\ X &= 1.0N\end{aligned}$$

In carrying out the titration, usually *burettes* are used to measure the volumes of the solutions accurately. A burette

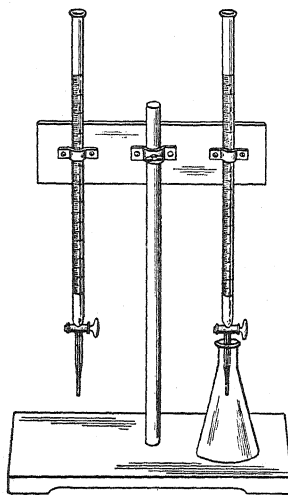


Fig. 15-2. Titration. Two burettes, one for acid and one for base, are used in a titration. These are calibrated to measure accurately the amount of solution delivered from the burettes.

is a long, slender tube with a delivery tube at the bottom end, which is accurately calibrated to show the quantity of solution delivered. If the solution stands at the mark on the burette for 5.00 milliliters and is allowed to run out until it stands at 10.00 milliliters, 5.00 milliliters of solution has been delivered.

The point at which the two solutions have exactly reacted with one another and where there is no excess of either solution is called the *end point* of the reaction. Chemists have devised a number of different methods for determining the end point of reactions, but the one which you will use in titrating acids and bases is the *indicator* method. An indicator is a colored organic compound which is a different color in acid and in base. You are familiar with litmus which is pink in acid solution and blue in base. Phenolphthalein is an indicator which is colorless in acid solution and magenta in basic solutions. Methyl orange is red in acid, yellow in base; congo red is blue in acid, red in base. There are many more indicators than these.

PROBLEM: Fifteen milliliters of a solution of acetic acid exactly reacts with 18.0 milliliters of 0.12*N* KOH. What is the normality of the acetic acid?

ANSWER:

$$15 \text{ ml.} \times XN (\text{HC}_2\text{H}_3\text{O}_2) = 18 \text{ ml.} \times 0.12N (\text{KOH})$$

$$X = 0.144N$$

When a titration is carried out, several determinations are made and the normality of the solution is calculated for each determination. If they check within about 1 per cent, the results are averaged. If one normality is very different from the others, it is discarded as an error. The reason for such precautions lies in the fact that everyone makes errors, and it can never be absolutely certain that on the first trial the right answer will be obtained. If, however, the experiment is repeated and the same answer is obtained, there is a strong probability that this is the true answer. It would be very difficult, indeed, to repeat an error in such a way that it would be exactly the same two consecutive times.

Home economists who are engaged in research or who are responsible for control or development in the food industry use quantitative procedures such as the titration. To determine

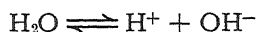
the amount of ascorbic acid (vitamin C) in orange juice, or whether or not a batch of vinegar comes up to specification, a titration is used. Titrations are used in clinical laboratories, in testing soils, and in many other fields allied to chemistry.

VERY DILUTE SOLUTIONS OF ACIDS AND BASES

The concentration of very dilute solutions of acids and bases is often expressed in terms of the concentration of the hydrogen or hydroxyl ion. The reason for this can be readily demonstrated. Very dilute solutions of acids and bases are important in foods, in medicine, in soils, etc. Frequently it is the physiological effect which is most important. If you taste a solution of 0.1*N* hydrochloric acid and one of 0.1*N* acetic acid, the sourness of the hydrochloric acid will be much greater than that of the acetic acid. The number of gram equivalent weights of acid will be the same, but since hydrochloric acid is a strong acid and acetic acid is weak, the quantity of hydrogen ions in the two solutions will be very different. The hydrochloric acid will have a great deal more hydrogen ions than the acetic acid solution. Your sensation of sourness has resulted from the hydrogen ions actually present and not from the concentration of acid or the potential hydrogen ions.

The Law of Mass Action and the Water Constant

In any water solution, there are both hydrogen and hydroxyl ions. This may be a startling concept to some of you. Water ionizes weakly to produce hydrogen and hydroxyl ions.



In a basic solution there will be a few hydrogen ions which are produced from the ionization of the water, and in an acid solution there will be a few hydroxyl ions produced from the water.

The ionization of water is an equilibrium reaction and, like all equilibrium reactions, the speed with which hydrogen ions combine with hydroxyl ions is exactly equal to the speed with which water molecules dissociate into hydrogen and hydroxyl ions. All equilibrium reactions obey the Law of Mass Action. The Law of Mass Action states that under controlled conditions the speed of a chemical reaction is directly proportional to the

molar concentration of the reactants. In other words, if a compound which contains hydrogen ions is added to water, the total concentration of the hydrogen ions will be increased and the rate with which hydrogen ions combine with hydroxyl ions will be speeded up.



Eventually a new equilibrium will be established, but in this case it will be farther to the left. Notice that there will still be an equilibrium and there will still be hydrogen and hydroxyl ions present. An increase in the concentration of one reactant may speed up the reaction in one direction and by this cause the equilibrium point to shift, but it cannot destroy the equilibrium. If an acid is added to water, the equilibrium point is shifted to the left and the concentration of hydroxyl ions is decreased. The concentration of the hydrogen ions produced by the ionization of water is also decreased, but since there are a large number present from the ionization of the acid, the *total* number of hydrogen ions in the acid solution is greater than in the pure water. Likewise, if a base is added to water, the concentration of the hydroxyl ions is increased, and the speed with which hydrogen and hydroxyl ions combine is increased until a new equilibrium is established. This equilibrium will also be shifted to the left and the number of hydrogen ions from the ionization of the water will be very small.

The Law of Mass Action is a mathematical law. That part of it will not be considered but only the water constant which is derived from it.

In any water solution, the product of the concentration of the hydrogen ion and the hydroxyl ion is a constant. This means that if these concentrations are measured under the same conditions of temperature, it is found that the product of these two numbers is always the same. Mathematically:

$$(\text{H}^+) \times (\text{OH}^-) = K_w$$

where (H^+) is the concentration of the hydrogen ion, (OH^-) is the concentration of the hydroxyl ion, and K_w is the constant. When the concentrations of the hydrogen and hydroxyl ions are measured in terms of moles per liter and when the temperature is 20°C ., the constant is 10^{-14} . This is known as the *water constant*.

$$\text{At } 20^\circ \text{C. } (\text{H}^+) \times (\text{OH}^-) = K_w = 1 \times 10^{-14}$$

Mathematics Review: You are more familiar with positive exponents than with negative exponents. You remember that a positive exponent such as 10^4 means that 10 is multiplied by itself four times.

$$10^4 = 10 \times 10 \times 10 \times 10$$

When the root is 10, it also means that the decimal point is moved from 1.0 four places to the right.

For 10^4 , 1.0 becomes 10,000

A number raised to a negative exponent is equal to the reciprocal of the same number raised to an equal positive exponent. Thus,

$$10^{-4} = \frac{1}{10^4} = \frac{1}{10 \times 10 \times 10 \times 10}$$

If the root is 10, you may write 1.0 and move the decimal point to the left the number of places in the exponent.

For 10^{-4} , 1.0 becomes 0.0001

In multiplying exponential numbers which have the same root, add the exponents.

EXAMPLES:

$$\begin{aligned} 10^{-3} \times 10^{-5} &= 10^{-8} \\ 10^{-2} \times 10^{-7} &= 10^{-9} \end{aligned}$$

In dividing exponential numbers which have the same root, subtract the exponent of the divisor from the exponent of the dividend.

EXAMPLES:

$$\begin{aligned} 10^{-6}/10^{-2} &= 10^{-6-(-2)} = 10^{-4} \\ 10^{-3}/10^{-7} &= 10^{-3-(-7)} = 10^{+4} \end{aligned}$$

It is very simple to calculate the hydrogen ion concentration or the hydroxyl ion concentration in any solution. In pure water all hydrogen and hydroxyl ions are produced from the ionization of water. Every time a molecule of water ionizes, it forms one hydrogen ion and one hydroxyl ion. Therefore, in pure water the hydrogen ion concentration is equal to the hydroxyl ion concentration.

$$(\text{H}^+) = (\text{OH}^-) = X$$

If the concentration of each of these ions is represented by X , then:

$$\begin{aligned} (\text{H}^+) \times (\text{OH}^-) &= 10^{-14} = X^2 \\ X &= 10^{-7} \text{ mole per liter} \end{aligned}$$

In pure water at 20°C. , the concentration of the hydrogen ion and the hydroxyl ion is 10^{-7} mole per liter or 0.0000001 mole per liter.

If an acid such as hydrochloric acid is added to the water until the solution is $0.1M$, the hydrogen ion concentration will

be enormously increased and the hydroxyl ion concentration will be decreased. What will they be? Hydrochloric acid is a strong electrolyte and in a $0.1M$ solution, the concentration of the hydrogen ion will be 0.1 mole per liter (actually it is 0.1 gram ionic weight per liter, but the term "moles" is used here too), plus that from the water. The hydrogen ion produced by the ionization of the water will be equal to the hydroxyl ion concentration. This is extremely small compared to the hydrogen ion produced from the acid and the quantity may be neglected in the calculation.

$$\begin{aligned}(\text{H}^+) &= 0.1 \text{ mole per liter} = 10^{-1} \\(\text{OH}^-) &= X \text{ moles per liter} \\(\text{H}^+) \times (\text{OH}^-) &= 10^{-14} \\&= 10^{-1} \times X \\X &= 10^{-14}/10^{-1} \\&= 10^{-13} \text{ mole per liter}\end{aligned}$$

You see that there is hydroxyl ion present in this acid solution, but at a very low concentration.

If a hydroxide such as sodium hydroxide is added to water, the hydroxyl ion concentration is markedly increased while the hydrogen ion concentration decreases. Suppose a $0.1M$ NaOH solution is prepared. Since sodium hydroxide is a strong electrolyte, the hydroxyl ion concentration will be 0.1 mole per liter. The hydrogen ion concentration will then be 10^{-13} mole per liter.

$$\begin{aligned}(\text{OH}^-) &= 0.1 \text{ mole per liter} = 10^{-1} \\(\text{H}^+) &= X \text{ moles per liter} \\(\text{H}^+) \times (\text{OH}^-) &= 10^{-14} \\&= X \times 10^{-1} \\X &= 10^{-13} \text{ mole per liter}\end{aligned}$$

pH

Chemists have devised a system for expressing these very low concentrations of hydrogen and hydroxyl ion concentrations. It is called pH and it is written with a small p and a capital H . The letters stand for the "power of the hydrogen ion concentration." The "power" of a number is its exponent. In using pH , the negative sign of the exponent is dropped. pH is, then, *the power of the hydrogen ion expressed as a positive number.**

* Mathematically $pH = \log \frac{1}{[\text{H}^+]}$, $[\text{H}^+]$ expressed as moles per liter.

pH TABLE

pH	H ⁺ conc.	OH ⁻ conc.
1	10 ⁻¹	10 ⁻¹³
2	10 ⁻²	10 ⁻¹²
3	10 ⁻³	10 ⁻¹¹
4	10 ⁻⁴	10 ⁻¹⁰
5	10 ⁻⁵	10 ⁻⁹
6	10 ⁻⁶	10 ⁻⁸
7	10 ⁻⁷	10 ⁻⁷
8	10 ⁻⁸	10 ⁻⁶
9	10 ⁻⁹	10 ⁻⁵
10	10 ⁻¹⁰	10 ⁻⁴
11	10 ⁻¹¹	10 ⁻³
12	10 ⁻¹²	10 ⁻²
13	10 ⁻¹³	10 ⁻¹

↑ C
I
D
I
C
A
C
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D
I
C
N E U T R A L
B
A
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↓

A pH of 1 or 2 represents a solution which is fairly strongly acid. As the pH increases, the solution becomes less and less acidic until finally at pH 7 it is neutral. As the pH rises above 7, the solution becomes more and more basic, until finally at pH 13 a strongly basic solution is produced. Notice that for each increase in the pH of one, there is a tenfold decrease in the hydrogen ion concentration. A pH of 3 represents a hydrogen ion concentration of 10⁻³ or 0.001 mole per liter, while a pH of 4 represents a hydrogen ion concentration of 10⁻⁴ or 0.0001 mole per liter. This is a tenfold decrease in the concentration of the hydrogen ion. A solution with a pH of 6 is acidic, but the concentration of hydrogen ion is very low. It is only 10⁻⁶ or 0.000001 mole per liter.

Methods of Determining pH Many methods of measuring the hydrogen ion concentration of solutions have been devised. The method which you will use depends upon indicators. You are already familiar with the fact that indicators are colored organic compounds which have a different color in acid solution from that which they show in basic solution. All indicators show gradual changes in color through a definite pH range. If, for example, methyl orange is added to an acidic solution, it will be red. If a dilute solution of base is carefully added to the acid, the color of the methyl orange will gradually change from

red through a salmon pink to orange, and then to yellow. There will be no sharp change from red to yellow. The range over which the indicator changes color comes over a pH range characteristic of each indicator. Methyl orange begins to change from red to salmon at pH 3.1, and it is not completely yellow until pH 4.4. Methyl orange is yellow in all basic solutions and even in those solutions which are faintly acid (pH 4.4 to 7.0). With relatively concentrated solutions of acids and bases methyl orange can be used to differentiate the acids from the bases, since all the acids will have a pH below 3. In very dilute solutions, methyl orange will be red if the pH varies from 0 to 3.1 and yellow for any pH above 4.4. Use of methyl orange can give the range of the pH of a solution, but it will take a battery of indicators to determine the pH with fair accuracy.

Suppose a solution of unknown pH gives a yellow color with methyl orange. This shows that the pH is above 4.4. Now the solution might be tested with phenolphthalein. If the solution remains colorless, this indicates that the pH is below 8.2. In other words, by the use of these two indicators, the possible pH has been narrowed down to between 4.4 and 8.2. An indicator with a color change in this range such as brom cresol purple would then be chosen. If this indicator turned purple in the

Color Changes of Some Indicators

<i>Indicator</i>	<i>Transition range in pH</i>	<i>Color</i>	
		<i>Acid</i>	<i>Alkaline</i>
Methyl violet	0.1– 3.2	Yellow	Violet
Methyl orange	3.1– 4.4	Red	Yellow
Methyl red	4.2– 6.3	Red	Yellow
Brom cresol purple	5.2– 6.8	Yellow	Purple
Brom thymol blue	6.0– 7.6	Yellow	Blue
Phenolphthalein	8.2–10.0	Colorless	Red
Thymolphthalein	9.3–10.5	Colorless	Blue

solution, it would show that the pH of the solution was between pH 6.8 and 8.2. For greater accuracy, another indicator would be used.

A mixture of indicators which have a different color for each step in the pH scale through the middle of the scale has been

developed and is known as Universal Indicator. The chief advantage of the use of Universal Indicator is the rapidity with which the approximate pH of a solution may be determined. One drop of the indicator mixture is added to a small volume of the solution and the color gives the approximate pH .

Universal Indicator

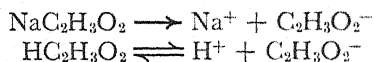
<i>Composition</i>	<i>pH</i>	<i>Color</i>
Thymol blue	4	Red
Methyl red	5	Orange
Brom thymol blue	6	Orange yellow
Phenolphthalein	7	Green
	8	Blue
	9	Indigo
	10	Violet

Buffer Systems A buffer system stabilizes the pH of a solution. If you add dilute hydrochloric acid to pure water or to some solution which does not contain a buffer, the pH will drop rapidly. Or if you add dilute sodium hydroxide to pure water, the pH will rise rapidly. However, if a buffer system is present, you can add either fairly large quantities of acid to the solution without the pH falling markedly or you can add a basic solution without the pH rising markedly. *A buffer system prevents marked changes in the pH of a solution on the addition of either acid or base.* A buffer system is composed of either the salt of a weak acid and that weak acid or the salt of a weak base and that weak base. Some examples of the first type of buffer system are sodium acetate and acetic acid, sodium bicarbonate and carbonic acid, potassium phosphate and phosphoric acid, or monosodium phosphate and disodium phosphate. Examples of the second type of buffer system are ammonium chloride and ammonium hydroxide or ammonium sulfate and ammonium hydroxide. The salt which forms one part of the buffer system is frequently called the *buffer* or the *buffer substance*.

A buffer system operates by reacting with the hydrogen ion of an acid or the hydroxyl ion of a base to form a poorly ionized molecule. Since it is only the hydrogen ions or the hydroxyl ions which influence the pH , the buffer system, by removing these

ions as they are introduced, stabilizes the pH until the buffer is used up.

A buffer system composed of a salt of a weak acid and that weak acid produces in solution a large number of cations and anions from the salt and a small number of hydrogen ions and anions from the acid. Salts are strongly ionized while the weak acid will, of course, be poorly ionized. In a buffer system of sodium acetate and acetic acid, there will be a large number of sodium and acetate ions and a small number of hydrogen ions.



When an acid is introduced into this solution, the acetate ions will combine with the hydrogen ions to form poorly ionized acetic acid. The ionization of acetic acid, which is weak at best, is depressed by the presence of the sodium acetate. This ionization follows the Law of Mass Action, as does the ionization of water. When a base is introduced into this solution, the hydrogen ions will combine with the hydroxyl ions to form water. Now the number of hydrogen ions is small and the number of hydroxyl ions with which they can combine is likewise small. But as soon as hydrogen ions are removed in this combination, the acetic acid will immediately ionize to produce more hydrogen ions which can neutralize more hydroxyl ions. The reactions are so rapid that there is no perceptible change in pH .

There are many applications of the principle of buffer action in the fields of biochemistry and nutrition, in food chemistry, in textiles and dyeing. The pH of the blood is remarkably constant because of the presence of a number of buffers in it. The maximum range is from pH 7.2 to 7.6. Yet the diet of normal people varies considerably in its acid-base balance. A high protein diet is usually predominantly acid forming. This means that the mixture of end products formed when a high protein diet is digested, absorbed, and then utilized by the cells is predominantly acid. This mixture of metabolic products is transferred from the cells to the blood. On the other hand, a high vegetable diet is predominantly base forming. The products of metabolism which are transferred to the blood from the cells after the utilization of the foods in a high vegetable diet are predomi-

nantly basic. Yet neither an acid-forming nor a base-forming diet alters the pH of the blood. The acid-base balance of the diet is of small importance, since the blood is equipped with buffer systems which can prevent a change in pH whether acid or base is added to the blood. The most important blood buffer system is composed of bicarbonate, principally sodium bicarbonate, and carbonic acid. This is so much more important than the other buffer systems that it is called the *alkali reserve* of the blood. The protein of the serum and the blood cells can act as a weak acid, and with it the potassium proteinate forms another buffer system. The other buffer is the monosodium phosphate and disodium phosphate of the blood.

Most acid foods contain buffer systems. Oranges contain citric acid, as well as sodium citrate, while tomatoes contain citric acid and malic acid and their salts. Proteins of food possess buffer action. When foods which contain buffer systems are ingested, they combine with the hydrochloric acid present in the gastric juice and buffer it. The food-gastric juice mixture has a pH approximately equal to that of the food until sufficient hydrochloric acid has been secreted to react with the buffers.

The buffering action of cow's milk is about three times as great as that of human milk. When an infant is fed cow's milk instead of human milk, the pH of the stomach contents is higher than normal and digestion may be poor. This is one of the problems of artificial feeding of infants. Often cow's milk is diluted so that the child will take a solution with a buffer content closer to that of human milk.

Other Applications of pH Protein molecules are very sensitive to the pH of the medium in which they are dispersed. If they are exposed to solutions with either high or low pH , they begin to change chemically and undergo the process of denaturation. Wool, silk, and hair or fur are composed primarily of protein, and any operation which involves solutions of either high or low pH are deleterious to the fibers. In dyeing these fibers, the pH of the dye bath is very carefully controlled so that the fibers do not harden and become brittle. In washing, it is likewise important that the pH of the wash water is kept as close to 7 as is practical. "Strong" soaps are soaps that give a pH as high as 10. They cannot be used with protein fibers with-

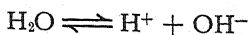
out damage to the fabric. You may have learned by experience that woolen sweaters must be washed in "mild" soap which has a pH closer to 7. The difference in the effect of "mild" and "strong" soap is due to the difference in the pH of the wash water.

Proteins are important in many cookery problems. Flour, eggs, milk, and meat contain protein, and the changes in these molecules are principally responsible for the success or failure of baked goods and cooked meat. The chemical change of the molecules which occurs in the presence of either high or low pH is accelerated as the temperature is raised. In a dough or batter, the protein of the flour, gluten, with some help from the protein in eggs and milk, forms the structural unit of the walls. If the pH of the batter is much above 7, the protein tends to crumble and the baked goods, therefore, tend to fall apart. If the pH is low, the protein tends to adsorb water, swell, and become tender. Cakes made with an excess of sour milk are very tender to bite or cut, but do not show much tendency to crumble. Meat cooked in tomatoes or vinegar becomes tender through the effect of the rather low pH . Tomatoes have a pH of 4.0 to 4.45, depending on the variety and growing conditions.

The pH of soil is one of the important factors in determining what type of vegetation will grow on it. "Acid" soil may have a pH as high as 6, yet most grasses and many flowering plants will not grow in it. Rhododendrons, azaleas, blueberries, and many other plants demand an acid soil for thrifty growth. Blueberries do best on a soil with a pH of 4.4. The "alkaline" soils of the world are famous for the poor, scanty vegetation which they support. Yet the pH is no higher in most than pH 8.5 to 11. In Palestine and in California there have been some experiments with alkaline soils in which the pH has been lowered by neutralization and leaching. When the pH is lowered, these soils support abundant vegetation.

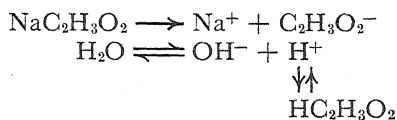
Hydrolysis of Salts

Some salts react with water to form a base and an acid. This is an example of an equilibrium reaction. Water ionizes to form hydrogen and hydroxyl ions.



An equilibrium exists, so that water molecules are continually dissociating to form hydrogen and hydroxyl ions and the ions are continually combining to form water. Since the speed with which these two ionic reactions take place is equal, the concentration of water, hydrogen ions, and hydroxyl ions never changes. In pure water every time a water molecule dissociates, it produces one hydrogen and one hydroxyl ion. The molecular concentration of hydrogen ions is equal to that of hydroxyl ions.

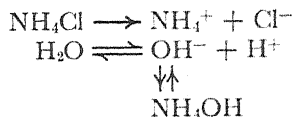
If a salt of a weak acid or of a weak base is dissolved in water, the situation is changed. The concentration of hydrogen ions and hydroxyl ions is no longer equal. Suppose that a salt of a weak acid and a strong base such as sodium acetate is dissolved in water. The salt forms sodium ions and acetate ions. The sodium ions show no tendency to associate with the hydroxyl ions since sodium hydroxide is a strong electrolyte and they are always dissociated. But the acetate ion does have a tendency to associate with (or react with) a hydrogen ion whenever they come in contact to form molecular acetic acid.



The concentration of the hydrogen ion falls. It can no longer react with the hydroxyl ion at the old rate, and for a very short time the speed of ionization of water molecules exceeds the speed of combination of the ions. The hydroxyl ion concentration exceeds the concentration of the hydrogen ion and is greater than it was in pure water. The solution is slightly basic.

The salt of a strong acid and a weak base will show a similar reaction except that it will be the positive ion which has a tendency to combine with the hydroxyl ion and the solution will, therefore, have an excess of hydrogen ions. It will be slightly acid. For example, ammonium chloride produces ammonium and chloride ions. In a water solution, the ammonium ion will have a tendency to combine with the hydroxyl ion although the chloride ion will not combine with the hydrogen

ion. The concentration of the hydrogen ion will thereby exceed the concentration of the hydroxyl ion.



Salts of weak acids or salts of weak bases react with water to form an acid and a base.

NEW TERMS

Molarity, normality, molar, molal, normal, gram equivalent weight, end point, indicator, titration, water constant, *pH*, buffer system, buffer substance, alkali reserve.

QUESTIONS

- Calculate the percentage of the solute in the following solutions: 5 grams of NaCl in 25 grams water, 3 grams of iodine in 75 grams alcohol, 25 grams of sucrose in 1 liter of water.
- Calculate the molarity and the normality of the following solutions: 500 milliliters of solution contains 24.5 grams H_2SO_4 ; 100 milliliters, 16 grams NaOH; 25 milliliters, 6.3 grams HNO_3 ; 10 milliliters, 3.05 grams CaCl_2 ; 2 liters, 296 grams H_3PO_4 ; 1 liter, 48.0 grams K_2CO_3 .
- Calculate the number of grams of solute in each of the following solutions: 200 milliliters $3N$ NaCl; 1 cubic centimeter $10N$ HCl; 1.5 liters $2N$ $\text{Ca}(\text{OH})_2$; 3 liters $1N$ $\text{HC}_2\text{H}_3\text{O}_2$; 150 milliliters $\frac{1}{2}N$ $\text{Mg}(\text{OH})_2$.
- Calculate the normality of the following acids from the titration data given.
 - 15 milliliters of $\text{HC}_2\text{H}_3\text{O}_2$ is exactly neutralized by 10 milliliters of $0.25N$ KOH.
 - 20 milliliters HCl is exactly neutralized by 25 milliliters $3N$ $\text{Ca}(\text{OH})_2$.
 - 15 cubic centimeters H_3PO_4 is exactly neutralized by 25 cubic centimeters $0.1N$ NaOH.
- What is the normality of a solution of silver nitrate in water if 15 milliliters is completely precipitated by reaction with 10 milliliters of $0.1N$ NaCl?
- Twenty-five cubic centimeters of a solution of BaCl_2 is completely precipitated by reaction with 10 cubic centimeters of $3N$ H_2SO_4 . What is the normality of the BaCl_2 ?

7. How many cubic centimeters of 0.2 normal hydrochloric acid can be neutralized by 25.10 of 0.15 normal sodium hydroxide?
8. How many cubic centimeters of 2 normal sodium carbonate solution will react with 80 cubic centimeters of 0.1 normal sulfuric acid?
9. How many liters of 0.25 normal acetic acid will be required to neutralize 2 liters of 0.125 normal sodium hydroxide?
10. How many cubic centimeters of 0.05 normal barium hydroxide solution will neutralize 40.5 cubic centimeters of 0.12 normal nitric acid?
11. If, in a titration, 24 cubic centimeters of a 0.5*N* sodium hydroxide solution will neutralize 36 cubic centimeters of a hydrochloric acid solution, what is the normality of the acid?
12. Calculate the normality of a solution of acetic acid from the fact that a volume of 22.5 cubic centimeters of the acid is neutralized by 35.2 cubic centimeters of a 0.2*N* base. Express the concentration of the acid in grams per liter.
13. In a titration experiment to determine the concentration of acetic acid in vinegar, 100 cubic centimeters of the vinegar required 16.4 cubic centimeters of a 0.25*N* solution of sodium hydroxide to neutralize it. Calculate the concentration of acetic acid in the vinegar in grams per 100 cubic centimeters.
14. Calculate the normality of a solution of sodium carbonate from the fact that a volume of 26.4 cubic centimeters is neutralized by 12.2 cubic centimeters of 0.5*N* acid. Determine the concentration of the sodium carbonate solution in grams per liter.
15. What is *pH*? Calculate the *pH* of a 0.001*M* HNO_3 solution.
16. What is the *pH* of a solution of 0.1*N* KOH ?
17. How may the *pH* of a solution be determined in the laboratory?
18. What is a buffer system? How do they function?
19. A solution which contains ammonium nitrate and ammonium hydroxide acts as a buffer. Explain how this mixture will protect the solution from an increase in hydrogen ion concentration; in hydroxide ion concentration.
20. Give two examples of buffer systems and explain in detail how each functions.
21. Give three applications of the concept of *pH*.
22. Which solution will have the higher *pH*—a solution which is 0.001*N* in acetic acid, or one which is 0.001*M* in hydrochloric acid? Why?
23. Which solution will have the higher *pH*—one which is 0.1*N* in H_2SO_4 , or one which is 0.1*N* in $\text{Ca}(\text{OH})_2$?
24. Which of the following salts will hydrolyze in water? Will the solution be acidic or basic? NaCl , K_2CO_3 , NH_4NO_3 , Na_3PO_4 , MgSO_4 , $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$.

Leavening Agents

A leavening agent is a substance or group of substances which react in a dough or batter to form tiny bubbles of gas and produce porosity. The tiny bubbles of gas are trapped in the dough or batter by its viscosity and elasticity. The dough or batter stretches around each little bubble, and if the mixture is properly balanced, it seldom breaks to release the gas. When the mixture is baked, more gas is formed at the higher temperature of the oven, the bubbles expand with the increased temperature, and the mixture "rises." The protein of the flour or of the egg and flour is denatured by the heat and sets the dough structure. Recipes must be designed so that the walls around each bubble are strong enough to stand when the product is removed from the oven and gas is compressed on cooling. The walls, however, must be tender enough to make it easy to bite through them.

If you have ever eaten unleavened bread, you know how important the leavening agent is to the success of the product. The common leavening agents and their reactions will be studied.

Steam

Steam operates as a leavening agent in all doughs and batters, but it is almost never the sole leavening agent. The effect depends on the enormous increase in volume which occurs when liquid water is changed to steam. One gram molecular weight of water is 18 grams. If this is vaporized at standard conditions, it would produce 22.4 liters of gas. At an oven temperature of 400° F., a hot oven, it will expand to 39.1 liters.

$$\begin{aligned} 400^{\circ} \text{ F.} &= 203^{\circ} \text{ C.} \\ &= 476^{\circ} \text{ A.} \end{aligned}$$

$$22.4 \text{ l.} \times 476^{\circ} / 273^{\circ} = 39.1 \text{ l.}$$

or 18 grams liquid = approximately 18 milliliters liquid = 39.1 liters of gas at 400° F. and 760 millimeters pressure. This is an increase of 18 to 39,100, or of one volume to 2170.

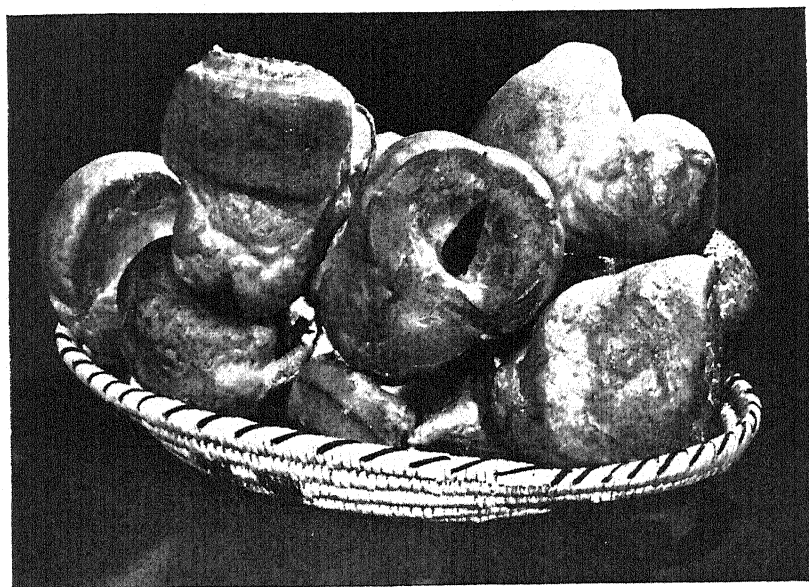
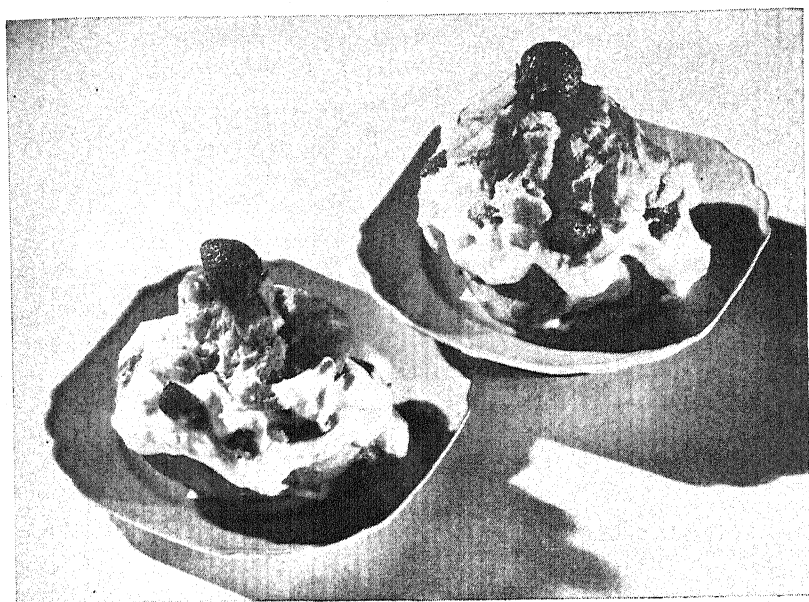


Fig. 16-1. Cream puffs and popovers are steam leavened. (Courtesy of General Mills Inc., Home Service Department.)

Popovers, cream puffs, and eclairs are leavened only by steam. All doughs and batters have fluid in them, and the liquid is water whether it is added as milk or in eggs or as water. As the water changes to steam, it puffs up the elastic dough and forms a thin-walled chamber.

Air

Air is a common leavening agent. It is incorporated into a batter during the creaming of the fat and sugar by beating and by the use of whipped egg white. Air is the leavening agent in angel cakes and sponge cakes and, to a limited extent, in butter cakes. When the batter is baked in the oven, the tiny bubbles of air expand and the cake rises. If the batter were completely elastic and there were no force to prevent expansion of the air bubbles, there would be an increase of volume of one and a half times. This is calculated by use of Charles' Law. If the temperature increases from a room temperature of 70° F. or approximately 21° C. (294° A.) to an oven temperature of 350° F. or approximately 178° C. (451° A.), we have:

$$1 \text{ vol. of air} \times 451^{\circ}/294^{\circ} = 1.53 \text{ vol. of air at } 178^{\circ} \text{ C. or } 350^{\circ} \text{ F.}$$

No batter is perfectly elastic, of course, and the expansion of the air bubbles is less than 1.5 times. The amount of expansion depends on the properties of the particular batter. However, there is always some expansion.

Yeasts and Bacteria

The oldest leavening agents are yeasts and bacteria. From ancient times, bread has been leavened with these microorganisms. Today a cake of yeast or a package of dried yeast can be bought and used to inoculate the dough. In a warm, moist environment, the yeast cells begin to grow. If there is nourishment in the environment, they will multiply rapidly. The old-fashioned way was to save a piece of the dough as a starter. Sometimes it was dropped into potato water. The "starter," which contained live yeast cells, was made up into a soft sponge, and when the yeast cells were growing rapidly, that is, when the sponge was rising, it was added to the dough. The chief disadvantage or advantage to this method was that the strains of yeast were sometimes contaminated with wild yeasts or other

microorganisms which produced definite flavors in the dough. If the flavor was desirable, the bread had a distinctive and delicious taste, but if the flavor was strong, or "off," this method was a definite disadvantage. Today, when most of you bake breads leavened with yeast only occasionally, the "starter" method is not practical. The yeast which you buy is carefully controlled so that other strains of yeast do not contaminate it.

When a yeast cell grows, it must have a wide variety of nutrients. One of these is carbohydrate in the form of the sugar glucose. The yeast cell produces a number of products, with ethyl alcohol and carbon dioxide in largest quantity. For many years the course of this reaction has been carefully studied, and it is now quite certain that the path from glucose to carbon dioxide and ethyl alcohol is

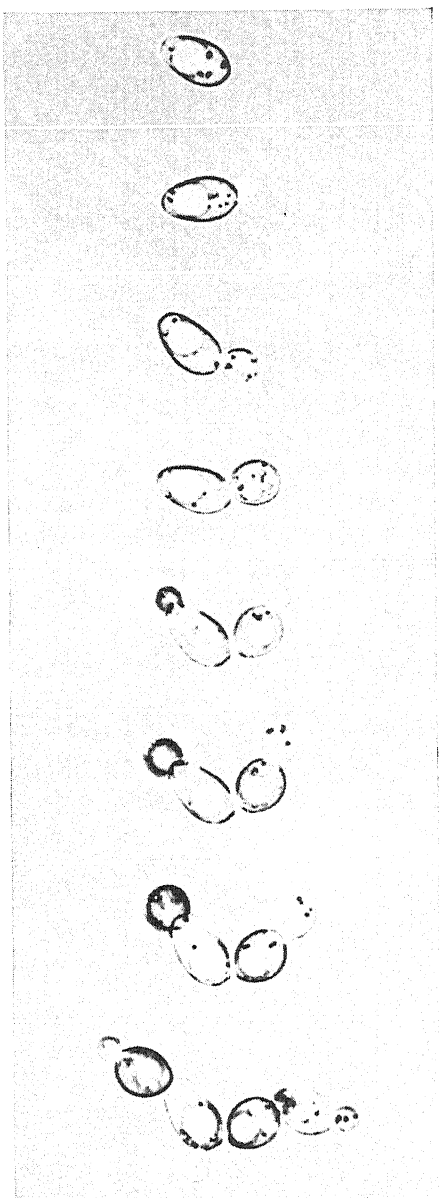
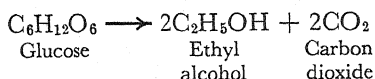


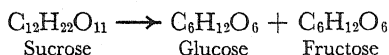
Fig. 16-2. Growth of yeast cells. Photomicrographs of the same yeast cell, taken at 1000 times magnification and at 30-minute intervals. (Courtesy Fleischmann Laboratories.)

a series of reactions. Almost every step in this series of reactions is catalyzed by enzymes, catalysts produced by the cell. The series of reactions is too complicated for us to study at the moment. It is identical, up to a point, with the reactions which occur when muscles contract. (See page 457.) The result of this series of reactions in the yeast cell is that one molecule of glucose is transformed into two molecules of ethyl alcohol and two molecules of carbon dioxide.



The carbon dioxide is a gas and leavens the dough. The ethyl alcohol is a liquid at room temperature with a high vapor pressure. It is largely vaporized in the baking and is the chief compound which gives odor to baking breads.

Most recipes for yeast doughs call for the use of sucrose, the carbohydrate in cane and beet sugar, rather than glucose. The sucrose is converted to glucose and fructose by an enzyme, which is present in yeast, and is commonly present in flours.



The glucose (and the fructose also) is then transformed into ethyl alcohol and carbon dioxide.

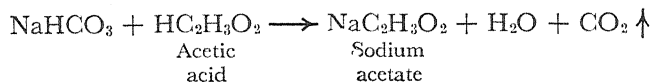
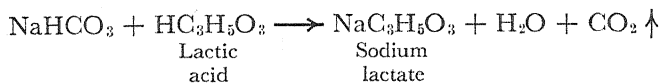
Bacteria are the microorganisms which are responsible for the distinctive flavor of "salt rising" bread and sour rye bread. Usually yeast is added to the dough as the leavening agent, and the dough is then exposed to the air for a relatively long period. In one recipe for sour rye bread, it is recommended that the sponge of rye flour, yeast, and water ferment for 18 to 20 hours. The other ingredients — white flour, molasses, salt, and caraway seed — are then added and a short fermentation period is used before baking. In your grandmother's time and for centuries before, salt rising bread was leavened with bacteria and some yeast. The sponge was either exposed to the air for inoculation or a "starter" was added. The salt was supposed to diminish the growth of undesirable organisms which would give the bread a strong odor. Today, commercial bakers can buy bacterial cultures for both "salt rising" bread and sour rye bread. They can then control the product.

Baking Soda

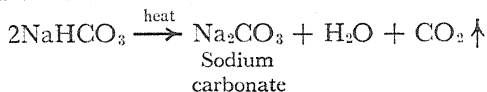
Baking soda is sodium bicarbonate, NaHCO_3 . In the presence of an acid, it reacts to form carbon dioxide and water. For example, sodium bicarbonate will react at room temperature with hydrochloric acid:



Hydrochloric acid is not used in doughs and batters, although Lowe reports that a baking powder was patented in 1837 which used hydrochloric acid. The acid used in most recipes is the lactic acid present in sour milk, the acetic acid present in vinegar, or the acids present in molasses. These all react with sodium bicarbonate to liberate carbon dioxide and leaven a batter.



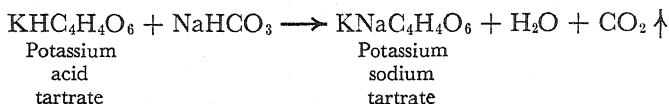
Neither sodium lactate nor sodium acetate leave objectionable flavors. The chief disadvantage of using soda and the acids present in sour milk or molasses is the variation in the amount of acid which occurs. Some "sour milk" may have very little acid developed in it, while other "sour milk" may have quite a lot. Excess acid will add a slight flavor to the product and will have a tenderizing effect. Most lactic or acetic acid is vaporized during baking. But excess soda is very objectionable. Sodium bicarbonate reacts on heating to form sodium carbonate, carbon dioxide, and water.



The carbon dioxide will leaven the product, and the sodium carbonate will remain in the mixture. Sodium carbonate has a strong, soapy, bitter taste, recognizable in even small amounts. Since sodium carbonate is the salt of a strong base and a weak acid, it will have a high $p\text{H}$. (See hydrolysis of salts, page 237.) This high $p\text{H}$ will make the product crumbly and may produce brown spots by reaction with the carbohydrates. Where chocolate or cocoa is used, the color will be reddish brown. Excess

soda is added to a Red Devil's Food Cake for this purpose, and the flavor is partly caused by the sodium carbonate in the baked cake. Despite the objections to the use of soda, there are still many recipes which use it, along with sour milk or molasses. Since excess acid is much less objectionable, and sometimes is desirable, recipes which call for soda may be modified by substituting baking powder for the soda. The quantity of baking powder used is usually one teaspoon for each cup of flour.

Some old recipes, developed before modern baking powders were available, use soda and cream of tartar. Cream of tartar is potassium acid tartrate, and since it is an acid salt of tartaric acid, and since tartaric acid is stronger than carbonic acid, it will react with sodium bicarbonate to form potassium sodium tartrate, carbon dioxide, and water.



The equation shows that one mole of potassium acid tartrate reacts with one mole of sodium bicarbonate. Since the molecular weight of potassium acid tartrate is 188 and that of sodium bicarbonate is 84, they will react in this proportion by weight. They have approximately the same density and will, therefore, react in the same proportion by volume; one teaspoon of cream of tartar will react with two and a quarter teaspoons of baking soda.

Modern Baking Powders

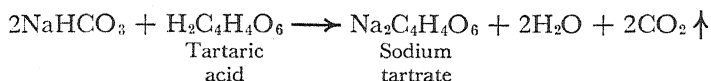
The baking powders on the market today are composed of baking soda, starch, and an acid salt or a mixture of acid salts. The baking soda and acid salts react in the moist medium of a batter or dough, and the starch is present to standardize the baking powder so that the same amount of leavening will be produced from one teaspoon of baking powder, no matter which one is used. The starch has some effect in keeping the baking powder dry and preventing reaction.

Lowé quotes Hart on the ideal baking powder: "The ideal baking powder (a) gives the most gas for the least volume and weight of the powder; (b) gives the gas slowly when cold and

increasingly in the cooking dough, so the dough may be mixed cold and left standing several hours; begins to generate gas in quantity in the oven and ceases to generate when it would rupture the crumb; (c) leaves a tasteless and absolutely harmless residue in the bread; (d) is cheap; (e) keeps well. The chemicals should not react on one another in the can and thus lose strength." No baking powder is absolutely ideal, but many available come close to it.

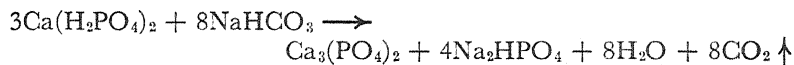
The baking powders available are either *tartrate*, *phosphate*, *sodium aluminum sulfate*, or *mixtures of these*.

Tartrate baking powders are a mixture of sodium bicarbonate, potassium acid tartrate (cream of tartar), and starch. Some have tartaric acid as well. The reaction for potassium acid tartrate and soda was given on the preceding page. Tartaric acid reacts according to this equation:



Both tartaric acid and potassium acid tartrate react rapidly with sodium bicarbonate when added to water at room temperature or to a moist batter or dough. The batter or dough must not be beaten excessively or allowed to stand for any length of time after the addition of the baking powder. If it is, much carbon dioxide will be lost and the product will not be properly leavened.

Phosphate baking powders which are available on the retail market contain monocalcium phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, as the acid salt, sodium bicarbonate, and starch. Some of the baking powders available in large-sized containers which may be used by bakeries have disodium pyrophosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, as the acid salt.

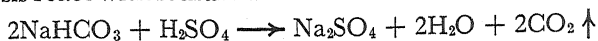


The monocalcium phosphate also reacts rapidly with sodium bicarbonate at room temperature in a moist medium, and batters must be mixed quickly and baked immediately.

Sodium aluminum sulfate is used in some baking powders to form acid on hydrolysis.



The sulfuric acid and the sodium acid sulfate formed by this hydrolysis react with sodium bicarbonate to release carbon dioxide.



The first reaction is very slow at room temperature, but is speeded up in the oven. The second reaction is rapid. This type of baking powder is very slow acting, and batters may be prepared and stored in a refrigerator for a day or even longer. The chief disadvantage of this type of baking powder is the residue of sodium sulfate, which is quite bitter. When SAS baking powders (sodium aluminum sulfate) first appeared on the market, there was considerable fear among many consumers that the aluminum would be poisonous. It was the same fear which accompanied the introduction of aluminum pans at reasonable prices at this time. Extensive studies were made on the toxicity of aluminum salts to animals and to man. There was never any indication that the use of SAS baking powders was in any way harmful.

Mixtures of sodium aluminum sulfate and phosphate baking powders are very common on the retail market. The phosphate is monocalcium phosphate. These baking powders are called "double action" since the phosphate reacts rapidly in the cold and the sodium aluminum sulfate reacts rapidly when heated. The quantity of sodium sulfate left as a residue is small and, therefore, not objectionable. This type of baking powder may be used when the batter will stand before baking. It is also fine for cooks who are slow.

If baking powders are stored in metal cans and the lids are kept tightly in place, the baking powders will last indefinitely. But if baking powder is exposed to moist air, it will slowly react and lose carbon dioxide. The powder usually cakes, so the cook can readily detect this action and discard the baking powder.

Some baking powders have very small amounts of egg albumin added to react with any moisture. The amount of egg white is so small that it does not affect the amount of egg used in the recipe.

NEW TERMS

Leavening agent, baking soda, cream of tartar.

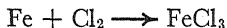
QUESTIONS

1. Why is steam a leavening agent? Calculate the volume which 1 gram of steam will occupy at 175° C. and 750 millimeters pressure.

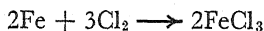
2. If 200 milliliters of air is beaten into the egg white used in an angel cake and if the batter is perfectly elastic, what increase in volume will occur when the cake is placed in a 325° F. oven after having been prepared in a 70° F. kitchen?
3. How can yeast leaven a loaf of bread?
4. What types of recipes use baking soda as the leavening agent? What difficulties are encountered in using baking soda? What substitution with baking powder can be made in these recipes?
5. What three types of baking powders are available in this country? What is the composition of each? What are the advantages and disadvantages of each? Give a balanced equation for the reaction which occurs when each baking powder is moistened.
6. Why are cream of tartar and baking soda used in some old-fashioned recipes?
7. What are the leavening agents in cream puffs? In rye bread? In sour rye bread? In butter cake? In sponge cake?

Oxidation Reduction Reactions

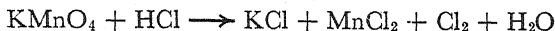
You have already studied some oxidation reduction reactions and you will remember that when an oxidation takes place, there is always a simultaneous reduction reaction. Some of the reactions which you have studied are simple reactions in that the unit number of molecules reacting and the unit number of molecules produced is small. Many oxidation reduction reactions involve a large unit of molecules in one reaction and the number and kind of molecules of product is large. You can easily balance a reaction which involves a small number of molecules by inspection. For example, the reaction of iron and chlorine to form ferric chloride is an oxidation reduction reaction which is quite easy to balance.



With the experience which you have gained in balancing simple equations, you can readily see that the balanced equation here is:



But when you come to a reaction, such as that which occurs between potassium permanganate and hydrochloric acid, balancing by inspection is very difficult and time consuming.



The balanced equation is:



Think how long it would take you by trial and error to work out this equation.

Oxidation is any chemical reaction in which there is a gain in positive valence or a loss of electrons.

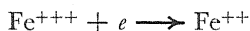
Reduction is any chemical reaction in which there is a loss of positive valence or a gain of electrons.

The two different definitions of oxidation and of reduction are really different ways of saying the same thing. The valence of an ion depends on the electrons. If an element has a valence of plus two, the free element has lost two electrons. This is the condition in magnesium, calcium, and ferrous ions, for example. If an ion has a valence of plus three, the free element has lost three electrons. Examples are the aluminum and the ferric ion. When the ferrous ion is changed to a ferric ion, and the valence changes from a plus two to a plus three, an electron must be lost.



Therefore, when it is said that oxidation is a gain in positive valence, it is saying that oxidation is a loss of electrons.

Likewise, if a ferric ion is changed to a ferrous ion, a reduction in positive valence from three to two, there must be a gain of an electron.



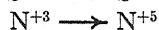
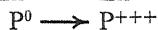
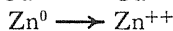
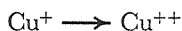
The electrons which are lost in oxidation are, of course, gained in the simultaneous reduction.

In an oxidation reduction reaction, the *number of electrons lost is equal to the number of electrons gained.*

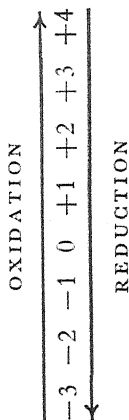
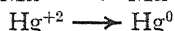
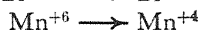
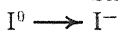
Examples of Oxidation and of Reduction

When an element changes in valence from plus two to plus three, it undergoes oxidation. And when an element changes valence from zero, the free state, to plus one, it likewise gains in positive valence and is oxidized. If a number scale is made, the number which comes below zero is minus one. This is followed by minus two, minus three, etc. If an element changes from minus one to zero, this is a gain in positive valence and is oxidation.

Examples of oxidation



Examples of reduction



Balancing Oxidation Reduction Equations

There are two general methods of balancing oxidation reduction reactions. Both will be described, but you will want to adopt only one method and use it exclusively. In balancing these equations, experience makes for ease of use. Balancing oxidation reduction reactions is something of a game with a few simple rules. When you learn the rules, you can play the game, but it is not until you have played a few times that you can go ahead without thinking through the rules at each step.

Method I: Electron Exchange In this method, all compounds are treated as if they were completely electrovalent. This is not true, but for the purpose of balancing equations by this method, they will be treated as if they were electrovalent.

(a) Determine the valence of all elements of the reactants and of the products. To do this, assume that hydrogen will always be plus one, except when it occurs as the free element. Assume that oxygen is always minus two, except when it occurs as the free element. Assume that sodium, potassium, and the other members of family 1A have a valence of plus one, and members of family 2A a valence of plus two. The reference elements as they occur in compounds are, then: H^+ , O^{--} , Na^+ , K^+ , Mg^{++} , Ca^{++} . You know the valences of other elements, of course, and these will help in figuring out the valence of the elements in some compounds. A compound is electrically balanced so that a molecule has no charge. The charge on the positive ions exactly neutralizes the charge on the negative ions. In HNO_3 , you know that the hydrogen is positive one and that each oxygen is negative two, or the three oxygens are negative six. $H^+N(O^{-2})_3^{-6}$. If the molecule is neutral, then the nitrogen must be positive five. $H^+N^{+5}(O^{-2})_3^{-6}$. Here are a few examples:

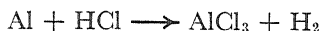
K_2CrO_4	$K_2^{++}CrO_4^{-8}$	Cr must be +6
HIO_3	$H^+IO_3^{-6}$	I must be +5
H_2SO_4	$H_2^{++}SO_4^{-8}$	S must be +6
PH_3	PH_3^{+++}	P must be -3

Use the valences that you already know. In the compound $MnSO_4$, the Mn, manganese, must have a valence of positive two, since the sulfate radical has a valence of minus two. When you establish this, you can then calculate that the sulfur must be positive six. $Mn^{++}SO_4^{-8}$. S is +6.

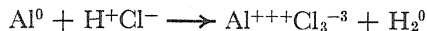
(b) Pick out the element which is oxidized in the reaction and the element which is reduced.

(c) Write supplementary equations which show the change in electrons for the element oxidized and the change in electrons for the element reduced. Balance these equations.

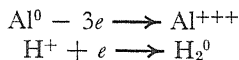
Here is a simple equation for an example and the same procedure will be followed with a more difficult one.



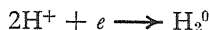
First the valence of each element is determined.



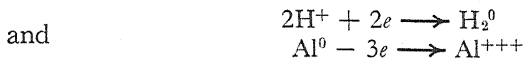
The aluminum changes valence from zero to positive three and is, therefore, oxidized. The hydrogen changes from positive one to zero and is, therefore, reduced. Chlorine is negative one on each side of the equation and, since it does not change valence, is not oxidized or reduced. The *supplementary equations* can now be written to show the electron change:



The last equation is not balanced, since there are two hydrogen atoms on the right-hand side of the equation and only one on the left-hand side.

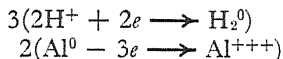


But now there are two hydrogen ions gaining electrons. The balanced supplementary equation is, therefore:



These are the balanced supplementary equations.

(d) Multiply the supplementary equations so that the number of electrons gained is equal to the number of electrons lost. Use the smallest numbers possible. In the equations, two electrons are gained by hydrogen ions and three electrons are lost by aluminum. The least common multiple of two and three is six. The supplementary equation for hydrogen must, therefore, be multiplied by three and the supplementary equation for aluminum multiplied by two.



Now there are six electrons gained by six hydrogen ions and six electrons lost by two aluminum atoms.

(e) Write the number of atoms or ions of each element into the main equation. Do not change the formulas and do not change these numbers once they are determined from the supplementary equation. For this reaction, the equation is:



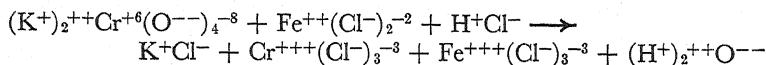
The supplementary equations have shown that there will be *six* hydrogen ions reacting to produce *three* molecules of hydrogen, H_2 , and that there will be *two* aluminum atoms producing *two* aluminum ions.

(f) In a simple equation, the other elements are balanced by inspection. In this equation the chlorine ions are the only other ones, and it can be seen that there are six on each side of the equation. It is, therefore, balanced.

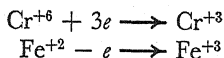
In more complicated equations, there is frequently a "solution agent." This is a molecule in which none of the elements change valence. The solution agent is balanced after the information from the supplementary equations is transferred to the main equation. A complicated equation will be balanced to demonstrate how to accomplish this.



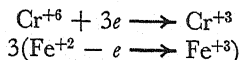
Determine the valence of all elements:



The elements which are changing valence are the chromium and the iron. Since no element in the hydrochloric acid changes valence, this molecule is the solution agent. The supplementary equations in balanced form are:



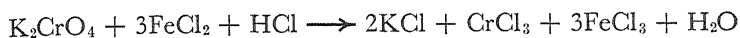
To make the number of electrons gained and the number lost equal, multiply the last equation by three:



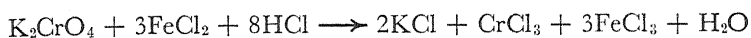
The information from the supplementary equations is transferred to the main equation; these show that one chromium will react with three ferrous ions to produce one chromium and three ferric ions.



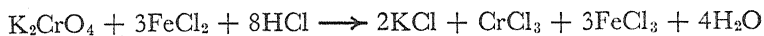
The other element which is established is potassium. Since there is only one molecule of K_2CrO_4 reacting with its one chromium, there are two potassium ions reacting, and there will be two potassium ions produced. This gives:



The solution agent is now balanced. Balance the chloride ions first and then do the hydrogen after that. There are fourteen chloride ions produced — two in 2KCl , three in CrCl_3 , and nine in 3FeCl_3 . Among the reactants, 3FeCl_2 will supply six chlorides. The other eight must come from the solution agent, the HCl . This means that eight molecules of HCl must be used.



The hydrogens can now be balanced. There are eight hydrogens on the left-hand side of the equation. Water is the only product containing hydrogen. There must be four molecules of water produced.



Now use the oxygen to check. If everything has been worked out correctly, there will now be the same number of oxygens on each side of the equation. In this equation there are 4 oxygens on each side of the equation.

A summary of the steps which are taken:

(a) Determine the valence of all elements of the reactants and products.

(b) Pick out the element which is oxidized and the element which is reduced.

(c) Write supplementary equations showing the electron change which these elements undergo and balance the supplementary equations.

(d) Multiply the supplementary equations so that the number of electrons gained is equal to the number of electrons lost. Use the smallest numbers possible.

(e) Transfer this information to the main equation.

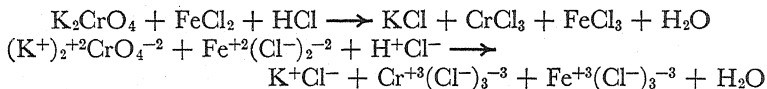
(f) Balance the solution agent.

(g) Balance the hydrogen

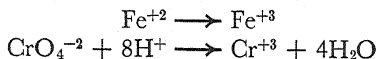
(h) Check the equation by counting the number of oxygen atoms on each side of the equation. They should be equal.

Method II: Ion Electron Change A second method of balancing oxidation reduction equations is the ion electron change. In this method the ions are used instead of the elements. Thus, if you are balancing an equation in which a radical, such as the chromate ion, CrO_4^{--} , is reduced, the whole ion is considered in the supplementary equations.

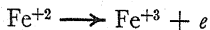
(a) Determine the valence of all the ions in the equation. For example, in the reaction of potassium chromate and ferrous chloride in the presence of hydrochloric acid, these are:



(b) Write two supplementary equations, one for the ion which is oxidized and one for the ion which is reduced. Balance them by adding water or hydrogen ions to the right- or left-hand side of the equation. For this reaction, write:

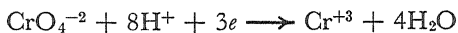


(c) Balance the supplementary equations electrically by adding electrons to either the right- or left-hand side of the equation. In the first supplementary equation, there is positive two on the left-hand side and positive three on the right-hand side. If an electron which is negative is added to the right-hand side, the equation will be balanced electrically.



The second supplementary equation has a negative two and a positive eight on the left-hand side. This makes a total value of positive six. The right-hand side has a positive three. If three

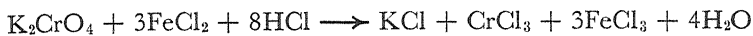
electrons are added to the left-hand side, the equation will balance electrically.



(d) Multiply the two equations by numbers which will make the number of electrons lost in one equation equal to the number gained in the other. Use the smallest numbers possible. In this case, we shall multiply the first equation by three.

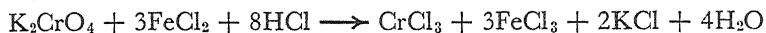


(e) Transfer the information from the supplementary equations to the main equations.



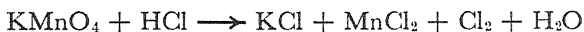
One supplementary equation shows that three ferrous ions react to form three ferric ions. The other supplementary equation shows that one chromate ion reacts with eight hydrogen ions to produce one chromium ion and four molecules of water. The eight hydrogen ions give us eight molecules of hydrochloric acid in the reaction.

(f) Balance the rest of the equation by inspection. The only elements which have not been considered so far are potassium and chlorine. Two potassium ions in the molecules of potassium chromate must give two molecules of potassium chloride.

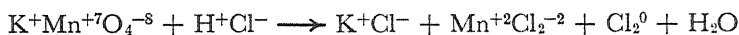


When the chloride ions are checked, it is seen that there are the same number on each side. The equation is balanced.

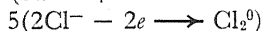
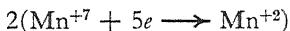
Another equation will be balanced by each method.



Method I

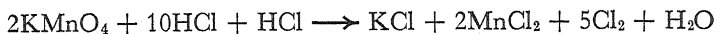


Supplementary equations:

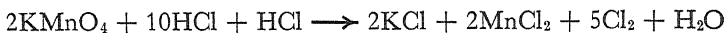


The information is transferred to the main equation. You will have noticed that, while some chloride ion is oxidized to free

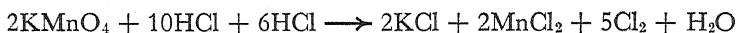
chlorine, other chloride ion does not change in valence. Some of the hydrochloric acid is acting as the reducing agent and is being oxidized, other hydrochloric acid is acting as the solution agent. These are separated in the main equation to make it easier to work with.



The other element is potassium. Since there are two on the left-hand side, there must be two on the right-hand side. This gives two molecules of potassium chloride.



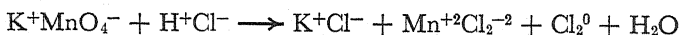
Now the solution agent is balanced by counting the chlorides on each side of the reaction. There are six chlorides on the right-hand side which have not changed in valence. Therefore, six molecules of solution agent are needed.



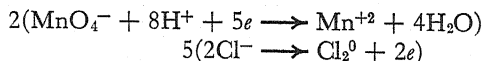
There are sixteen hydrogens on the left-hand side of the equation; therefore, there will be eight molecules of water on the right-hand side. Checking the oxygen it can be seen that there are eight on each side of the equation. The two hydrochloric acids, the molecules which are reducing agent and the molecules which are solution agent, can now be added:



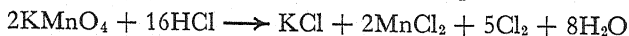
Method II



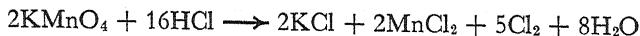
Supplementary equations:



Transferring this information to the main equation:



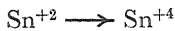
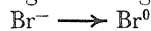
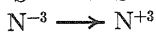
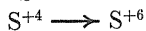
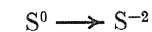
The element which has not been balanced is potassium. Therefore,



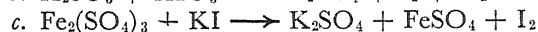
When the chlorides are counted, it is found that there is the same number on each side of the equation. The equation is balanced.

QUESTIONS

1. Define oxidation, reduction, oxidizing agent, reducing agent.
2. Which of the following changes in valence are oxidation, which are reduction?



3. Determine the valence of all elements in the following compounds:
 H_2SO_4 , HNO_3 , HNO_2 , H_2SO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, Cu_2Cl_2 , HIO_3 , HClO_4 ,
 HBr , HBrO .
4. Write an example of each of the four types of simple equations:
 addition, substitution, decomposition, and double decomposition.
 Pick out the reactions which are oxidation reduction reactions and
 explain why you have designated them this way.
5. Why does a free element such as copper or chlorine, Cl_2 , have a
 valence number of zero?
6. Balance the following simple chemical reactions by one of the
 methods for balancing oxidation reduction equations:
 - a. $\text{CuSO}_4 + \text{Fe} \longrightarrow \text{Cu} + \text{FeSO}_4$
 - b. $\text{Zn} + \text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2$
 - c. $\text{AlI}_3 + \text{Cl}_2 \longrightarrow \text{AlCl}_3 + \text{I}_2$
 - d. $\text{Fe} + \text{Cl}_2 \longrightarrow \text{FeCl}_3$
 - e. $\text{H}_2\text{S} + \text{O}_2 \longrightarrow \text{SO}_2 + \text{H}_2\text{O}$
 - f. $\text{Ag} + \text{AuCl}_3 \longrightarrow \text{AgCl} + \text{Au}$
 - g. $\text{SnCl}_2 + \text{FeCl}_3 \longrightarrow \text{SnCl}_4 + \text{FeCl}_2$
 - h. $\text{FeBr}_3 + \text{Cl}_2 \longrightarrow \text{FeCl}_3 + \text{Br}_2$
 - i. $\text{Br}_2 + \text{H}_2\text{S} \longrightarrow \text{HBr} + \text{S}$
 - j. $\text{H}_2\text{SO}_4 + \text{HBr} \longrightarrow \text{H}_2\text{O} + \text{Br}_2 + \text{SO}_2$
 - k. $\text{C} + \text{H}_2\text{SO}_4 \longrightarrow \text{CO}_2 + \text{SO}_2 + \text{H}_2\text{O}$
 - l. $\text{Pb}_2\text{O}_3 + \text{HCl} \longrightarrow \text{PbCl}_2 + \text{Cl}_2 + \text{H}_2\text{O}$
 - m. $\text{PbO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{PbSO}_4 + \text{H}_2\text{O} + \text{O}_2$
 - n. $\text{FeCl}_3 + \text{TiCl}_3 \longrightarrow \text{FeCl}_2 + \text{TiCl}_4$
 - o. $\text{MnO}_2 + \text{HCl} \longrightarrow \text{MnCl}_2 + \text{Cl}_2 + \text{H}_2\text{O}$
7. Balance the following more complicated oxidation reduction equa-
 tions.



- d. $\text{Al}_2(\text{SO}_4)_3 + \text{KI} + \text{KIO}_3 + \text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 + \text{K}_2\text{SO}_4 + \text{I}_2$
e. $\text{H}_3\text{SbO}_4 + \text{HI} \longrightarrow \text{H}_3\text{SbO}_3 + \text{H}_2\text{O} + \text{I}_2$
f. $\text{Sb}_2(\text{SO}_4)_3 + \text{KMnO}_4 + \text{H}_2\text{O} \longrightarrow$
 $\text{H}_3\text{SbO}_4 + \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{H}_2\text{SO}_4$
g. $\text{H}_3\text{AsO}_3 + \text{Ba}(\text{BrO}_3)_2 \longrightarrow \text{H}_3\text{AsO}_4 + \text{BaBr}_2$
h. $\text{KClO}_3 + \text{HI} + \text{H}_2\text{SO}_4 \longrightarrow \text{KHSO}_4 + \text{HCl} + \text{H}_2\text{O} + \text{I}_2$
i. $\text{Cu}_2\text{O} + \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{FeSO}_4 + \text{H}_2\text{O}$
j. $\text{MnO}_2 + \text{FeSO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{MnSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$
k. $\text{Mn}(\text{NO}_3)_2 + (\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} \longrightarrow$
 $(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{HNO}_3 + \text{HMnO}_4$
l. $\text{Cu} + \text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO}_2 + \text{H}_2\text{O}$
m. $\text{Cu} + \text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO} + \text{H}_2\text{O}$
n. $\text{FeSO}_4 + \text{HNO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{N}_2\text{O}_3 + \text{H}_2\text{O}$
o. $\text{KMnO}_4 + \text{HNO}_2 + \text{H}_2\text{SO}_4 \longrightarrow$
 $\text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{HNO}_3 + \text{H}_2\text{O}$
p. $\text{KHSO}_3 + \text{I}_2 + \text{H}_2\text{O} \longrightarrow \text{K}_2\text{SO}_4 + \text{HI} + \text{H}_2\text{SO}_4$
q. $\text{K}_2\text{S}_2\text{O}_8 + \text{FeSO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4$
r. $\text{Na}_2\text{S}_2\text{O}_3 + \text{NaMnO}_4 + \text{H}_2\text{O} \longrightarrow \text{Na}_2\text{SO}_4 + \text{MnO}_2 + \text{NaOH}$
s. $\text{HNO}_3 + \text{Al} + \text{KOH} \longrightarrow \text{NH}_3 + \text{KAlO}_2 + \text{H}_2\text{O}$
t. $\text{HNO}_3 + \text{PbS} \longrightarrow \text{PbSO}_4 + \text{NO} + \text{H}_2\text{O}$

The Nonmetals

The nonmetals are a group of elements which are of great importance in our daily life. Bleaches and washing compounds, medicinals and dye precipitants are among the many useful compounds formed by the nonmetals. They have been briefly discussed in Chapters 6 and 10.

The nonmetals are the group of elements in the upper right-hand portion of the Periodic Table. They are the elements in groups 5, 6, and 7 which have rather low atomic weights — the members of the nitrogen family, the sulfur family, and the halogens. Chemically these elements are “acid formers.” Their oxides react with water to form oxygen acids and many of the hydrides are acids. In compounds, these elements usually either form the negative ion or are part of the negative radical. Physically some exist at room temperature as gases; one, bromine, is a liquid; and a few are solids. None has any of the physical characteristics which are associated with metals — luster, ductility, malleability, or hardness.

THE HALOGENS

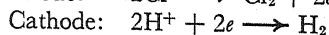
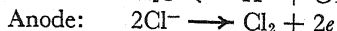
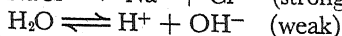
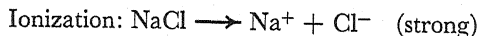
The halogens are a family of elements in group 7 which show close family resemblance and includes the four elements fluorine, chlorine, bromine, and iodine. The name “halogen” means “salt former.” None of the elements occurs free in nature, but all are widely distributed in the form of their salts. Since most of their salts are soluble, the halogen compounds have been well removed from the soil through the centuries of leaching by rain water, and are concentrated in the ocean. There are many deposits of halogen compounds that are undoubtedly the residue of old seas. Some of these deposits are in the form of brines or water solutions of these salts.

Chlorine

The free elements have been known only since the rise of the science of chemistry, although some salts, such as sodium chloride, were used in the ancient world. Chlorine was first discovered by the remarkable Swedish apothecary, Karl Wilhelm Scheele (1742–1786), who discovered and studied the properties of a great many compounds, both inorganic and organic, which are familiar now. He prepared chlorine when he treated a mineral which contains manganese dioxide with hydrochloric acid. He was interested and impressed by the yellow green gas, but it was not until years later that Davy proved that chlorine is an element.

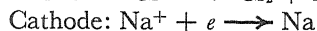
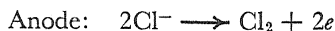
At room temperature, chlorine is a greenish yellow gas with a strong irritating odor. When it is inhaled, even in dilute solutions in air, it causes a stinging sensation in the throat, nose, and eyes, followed by coughing as a watery discharge comes over these delicate membranes. You are all familiar with its odor in very dilute amounts, since it is commonly used as a disinfectant in swimming pools.

Commercially, chlorine is prepared from the electrolysis of either molten chloride or of the aqueous solution of sodium chloride. Brine is sometimes pumped directly from salt wells into huge electrolyzers. The chloride ion of the sodium chloride moves to the anode or positive pole of the electrolytic cell, while the sodium ion of the sodium chloride and the hydrogen ion from the water move to the cathode or negative electrode. The chloride ions give up electrons and form free chlorine. At the cathode, the hydrogen ion is more readily discharged than the sodium ion, and it accepts an electron and forms free hydrogen. The sodium ions and hydroxide ions from the water remain in the solution.

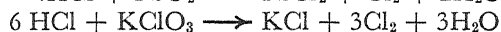
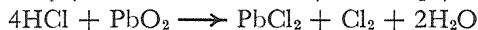


If solid sodium chloride is melted and electrolyzed, the chlorine ions move to the anode and lose electrons to form free

chlorine. The sodium ions move to the cathode and accept electrons to form free sodium.

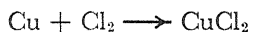


Chlorine may be prepared in the laboratory by the oxidation of chlorides with such oxidizing agents as manganese dioxide, MnO_2 , potassium permanganate, KMnO_4 , lead dioxide, PbO_2 , and potassium chlorate, KClO_3 . The chloride ion is oxidized to free chlorine.



Chemical Properties Chlorine is an active element which combines directly with many elements.

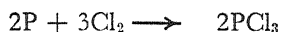
1. It combines with both metals and nonmetals. The metallic chlorides are electrovalent compounds, while the nonmetallic chlorides are covalent.



Copper
chloride



Hydrogen
chloride



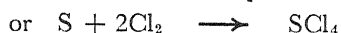
Phosphorous
trichloride



Phosphorous
pentachloride

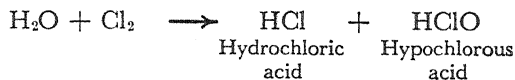


Sulfur
monochloride



Sulfur
tetrachloride

2. Chlorine reacts with water to form two acids or with hydroxides to form the salts of these acids.



Hydrochloric acid Hypochlorous acid

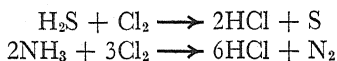


Sodium chloride Sodium hypochlorite

When chlorine is passed into water, the mixture which is formed is frequently called "chlorine water," as if the action were simply

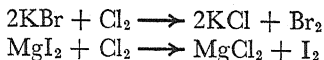
one of solution. "Chlorine water" contains, however, the two acids, hydrochloric and hypochlorous, and the reactions of each acid are given by the solution. There is always some free chlorine in the solution, and the reactions of this element are given by it. "Chlorine water" has the odor of chlorine. The reaction is evidently an equilibrium reaction. The solution which is produced when chlorine is passed into a hydroxide has strong bleaching action on cotton and is the most widely used bleaching agent in the home. When the hydroxide is potassium hydroxide, it is commonly called "javelle water," since it was first prepared in 1792 near Paris at a chemical works in Quai de Javelle. Chlorinated sodium hydroxide is sold under the brand names of "Clorox," "Purex," "White Sail Bleach," "Roman Cleanser," "Zonite," and others.

3. Chlorine reacts with some compounds as an oxidizing agent, when it is usually reduced to a valence of minus one.



4. Chlorine acts on moist cotton, straw, wood pulp, and paper as a bleaching agent. The reaction is probably due to the formation of hypochlorous acid, HClO , which is a strong oxidizing agent. Colored compounds which are changed to colorless molecules on oxidation disappear from the material which is bleached. Not all colored compounds form colorless substances on oxidation, and those which do not are not affected by the bleaching action of chlorine.

5. Chlorine reacts with bromides and iodides to replace the halogen in the compounds, since chlorine is a stronger oxidizing agent than either bromine or iodine.

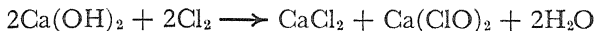


The Oxygen Acids of Chlorine Chlorine forms a series of oxygen acids.

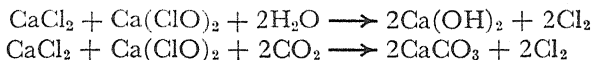
<i>Formula</i>	<i>Name of acid</i>	<i>Name of salt</i>
HClO	Hypochlorous acid	Hypochlorite
HClO_2	Chlorous acid	Chlorite
HClO_3	Chloric acid	Chlorate
HClO_4	Perchloric acid	Perchlorate

All these acids are strong oxidizing agents. You are familiar with the potassium salt of chloric acid, potassium chlorate, KClO_3 , which is commonly used in the laboratory preparation of oxygen.

Bleaching Powder Bleaching powder has been widely used as a household disinfectant. It is still commonly called "chloride of lime" although it is primarily a mixture of the calcium salts of hydrochloric and hypochlorous acids, and calcium hydroxide. It is prepared by passing chlorine over calcium hydroxide.



Crude calcium hydroxide (slaked lime) is used and no attempt is made to purify the product. It is as useful in the home in the crude state as if it were purified and is much cheaper. Bleaching powder is now available which is called HTH (the letters stand for "high test hypochlorite") and this product is straight calcium hypochlorite, $\text{Ca}(\text{ClO})_2$. Since the action of bleaching powder depends on the hypochlorite content, HTH is much more effective as a disinfectant than "chloride of lime." The odor of chlorine can be readily detected over either bleaching powder or HTH, and any material in an open can will slowly decompose.



Raw cotton and linen have a grayish yellow color which is usually bleached out by the action of hypochlorite before the goods are finished. The wax and tannins are removed from the cloth by passing it through a dilute solution of sodium hydroxide (caustic soda), washing, and acidifying to remove any residual hydroxide. The bleaching is carried out by passing the cloth through a solution of either calcium, sodium, or potassium hypochlorite. It must then be washed, dipped in a dilute acid solution, and washed again. The bleaching agent tenderizes the fibers of linen and cotton so that the tensile strength is lowered. After many launderings, the yellow color gradually returns to the fabric. In laundries and in many homes, bleaching solutions are regularly used to maintain the whiteness of cotton and linen. It is extremely important that all the bleaching solution be completely removed so that loss of tensile strength will be at a minimum. In laundries it is customary to pass the bleached clothes

through an "antichlor," a substance such as sodium thiosulfate which reacts with and destroys the bleach.

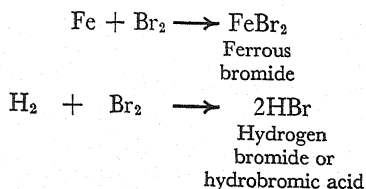
Chlorine and the hypochlorites are excellent disinfectants and have been used for this purpose for many years in the homes of America. A "disinfectant" is a substance which kills microorganisms. Chlorine and the hypochlorites are effective in low concentrations. They are used to make water safe for drinking, to disinfect dishes and eating utensils when a contagious disease occurs, and to disinfect privies. During World War II, troops were supplied with small packets of hypochlorites to add to water before it was drunk. The remarkable absence of infectious diseases during the war was the direct result of the vigilance of the armed forces. One of their precautionary measures was the use of hypochlorites.

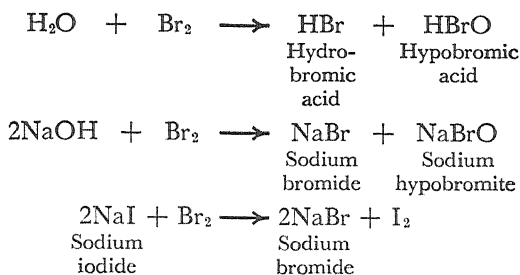
Bromine

Bromine is a dense brown liquid at room temperature with a specific gravity of 3.19 at 0° C., and a boiling point of 58.7° C. at 760 millimeters pressure. It has a high vapor pressure at room temperature, and the liquid is always blanketed with a dark brown cloud of gaseous bromine. It has an odor similar to chlorine and is, if anything, more irritating to the mucous membranes of the nose, throat, and eyes.

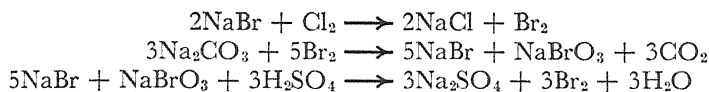
Bromine was discovered in 1826 in sea water by Balard. It was prepared by treating sea water with chlorine. The bromides were replaced with chloride and free bromine liberated. This method is still used.

Chemically, bromine is similar to chlorine, but it is not as strong an oxidizing agent. It reacts with many elements, with water, and with hydroxides to form compounds analogous to those of chlorine. It is a stronger oxidizing agent than iodine and will replace iodine from iodides.





Commercially bromine is important because it is used to synthesize an intermediate in the production of lead tetraethyl. Lead tetraethyl is an antiknock agent which is added to most gasoline, both "regular" and "ethyl." When it was discovered that lead tetraethyl is such an excellent antiknock agent, the bottle neck in its production came in the scarcity of bromine. But Dow Chemical Company had perfected a method for isolating bromine from brines, and it was easily expanded to produce as much bromine as is necessary in the manufacture of lead tetraethyl. Bromine is now extracted from sea water, although the concentration of bromides is less than 70 parts per million. The sea water is acidified and sprayed into chlorine gas. The chlorine replaces the bromine in the bromides and the bromine is released as a gas. This gas is absorbed in sodium carbonate and stored in that form until it is needed. It is released from the carbonate solution by acidification with sulfuric acid.

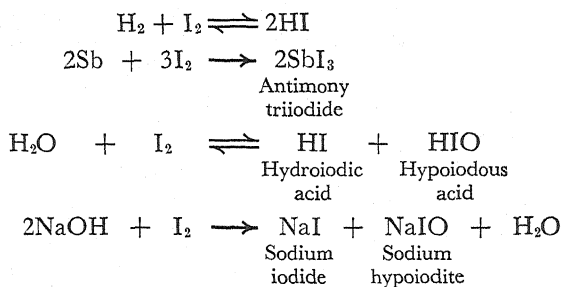


Iodine

Iodine was discovered in 1812 by the French chemist Courtois when he treated seaweeds with sulfuric acid. It is a purplish black solid that forms large, easily broken crystals. The solid has a high vapor pressure. Even at room temperature, the purple gas may be seen above the crystals in a stoppered bottle. If a bottle is left unstoppered, the crystals soon disappear through evaporation. The solid will *sublime* and may be separated from nonvolatile impurities by this process. The solid is warmed, and the gas produced is cooled on a clean surface. Long crystals of

pure iodine grow rapidly. Iodine is very slightly soluble in water to form a brown solution. It is more readily soluble in carbon disulfide, carbon tetrachloride, and ethyl alcohol. It has an odor similar to bromine and chlorine and, like them, is irritating to the mucous membranes. A concentrated solution of iodine in alcohol can cause severe burns on the skin.

Chemically, iodine is similar to chlorine and bromine. It is not as strong an oxidizing agent as either chlorine or bromine and will, therefore, not react with either chlorides or bromides. It will react with metals, water, and bases, although not as rapidly or as extensively as chlorines and bromine.



SULFUR

Sulfur is one of the few nonmetals which was known to the ancient world. It is the "brimstone" of the Bible and was still called by that name in ordinary commerce fifty years ago. The fact that sulfur occurs as a free element in the earth, a crust near volcanic areas, accounts for man's early knowledge of the substance. However, sulfur was not recognized as a true element until the rise of chemistry in recent times.

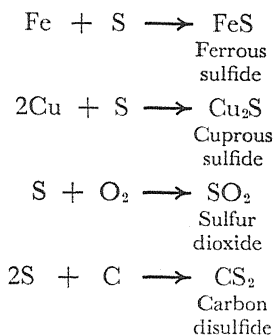
Besides the sulfur which occurs free in nature, sulfur occurs in a number of minerals which are sulfides and a few that are sulfates. Some important ores which contain metallic sulfides are pyrites, FeS_2 , cinnabar, HgS , galena, PbS , and zinc blende, ZnS , while gypsum contains calcium sulfate, CaSO_4 , and heavy spar, barium sulfate, BaSO_4 . Sulfur is also present in sea water in the form of soluble sulfates.

Sulfur is produced very cheaply in this country by the Frasch process from the huge deposits of free sulfur in Louisiana. A casing composed of three concentric tubes is sunk into the earth until it is in contact with the free sulfur. Superheated steam is

forced through the outer tube, and air through the middle tube. The sulfur melts at the temperature of the superheated steam and the compressed air forces it to rise in the inner tube. Molten sulfur is poured into large yards where it hardens. It is loaded directly from these yards into box cars for shipment to industries all over the United States.

Sulfur occurs in several crystal forms. The property of an element to exist in several crystal forms is called allotropism and the forms are called allotropic forms. As molten sulfur hardens, it forms rhombic sulfur with the crystals "kite shaped." This is the most common form of sulfur. If sulfur is crystallized above 95.5°C ., it forms long needles of monoclinic sulfur. This form slowly changes back to rhombic sulfur. When sulfur sublimes, it forms very finely divided sulfur which is not crystalline. This is amorphous sulfur and is known as "flowers of sulfur." It is the sulfur which is commonly used in medicinals, such as ointments or as a powder for application to the skin. The fourth form of sulfur is brown plastic sulfur. This is produced by heating sulfur above its melting point and pouring it into cold water. The yellow sulfur changes to a brown, gummy liquid, and when it is chilled, its appearance is much like rubber. The plastic sulfur is elastic and moldable, but on standing it slowly crystallizes in the rhombic form.

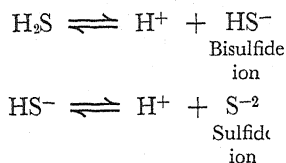
Chemical Properties Sulfur is a fairly active element. It combines directly with many metals to form sulfides and with such nonmetals as oxygen and carbon.



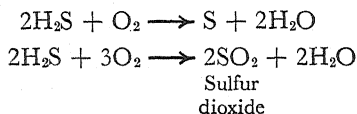
Hydrogen sulfide is one of the common compounds of sulfur. It is a gas at room temperature and has a strong, characteristic

odor which is always described as "like rotten eggs." It is true that when eggs spoil, hydrogen sulfide is produced along with other gases, and it is the one with the dominant odor. However, it is also formed from the putrefaction of most other proteins. Hydrogen sulfide is the gas which is present in natural waters called "sulfur water" and which gives it its strong, disagreeable odor. Many other mineral waters contain small traces of hydrogen sulfide, while the hot springs and geysers in volcanic areas may contain appreciable quantities.

Hydrogen sulfide acts as a very weak acid to produce a hydrogen ion and a bisulfide ion. The bisulfide ion is more weakly ionized to produce a hydrogen ion and a sulfide ion.

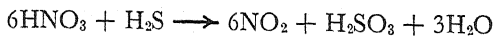


It reacts with oxygen to form free sulfur or sulfur dioxide.



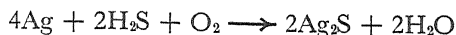
This reaction occurs to a limited extent with atmospheric oxygen. Around many of the hot pools in Yellowstone Park, deposits of yellow sulfur have formed which add much color and beauty to them by the oxidation of hydrogen sulfide carried up in the hot water. Sulfur dioxide can also be detected easily in the atmosphere around many of the hot springs. The odor of the Norris Geyser Basin, which can be smelled for a considerable distance from the basin, is a mixture of the odor of hydrogen sulfide and sulfur dioxide.

Hydrogen sulfide reacts with oxidizing agents as a reducing agent. It is sometimes oxidized to sulfur, to sulfur dioxide, SO_2 , to sulfite, SO_3^{2-} , or even to sulfate, SO_4^{2-} .



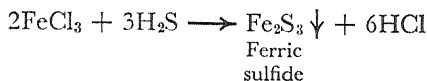
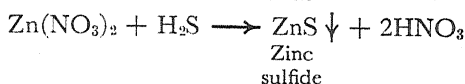
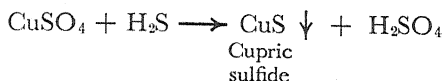
It will react with a metal such as silver in the presence of air as an oxidizing agent. The rapid formation of tarnish on silverware

in smoky cities is the result of the action of small amounts of hydrogen sulfide in the coal smoke with the silver. The course of the reaction is believed to be:

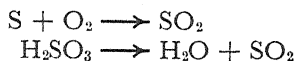


The reaction is not a simple replacement of hydrogen by silver, since silver is so far below hydrogen in the Electromotive Series.

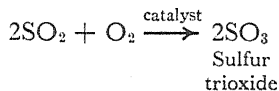
Hydrogen sulfide reacts with the soluble salts of many metals to form sulfides. Many of these are difficultly soluble, and some of the colors are characteristic of the metal. The sulfides are frequently used as a means of separating and identifying the different metal ions. This accounts for the almost constant odor of hydrogen sulfide around qualitative analysis laboratories.



Sulfur forms four oxides: sulfur dioxide, SO_2 , sulfur trioxide, SO_3 , sulfur sesquioxide, S_2O_3 , and sulfur heptoxide, S_2O_7 . Sulfur dioxide and sulfur trioxide are the common ones. Sulfur dioxide is formed by the burning of sulfur in air or oxygen, or by the decomposition of sulfurous acid.



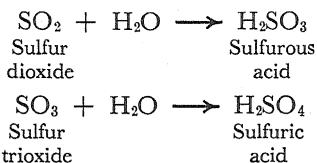
Only small traces of sulfur trioxide are formed, even when sulfur is burned in pure oxygen, but sulfur dioxide and oxygen will combine to form the trioxide in the presence of some catalysts.



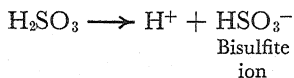
Sulfur trioxide is also formed when sulfuric acid is decomposed by heating it strongly.



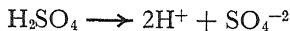
Both of these oxides are acid anhydrides: they form oxygen acids with water. Sulfur dioxide forms sulfurous acid, a weak acid, while sulfur trioxide forms sulfuric acid, which is strong.



Sulfurous acid ionizes to produce hydrogen ions and bisulfite ions, and the bisulfite ionizes to produce hydrogen ions and sulfite ions.



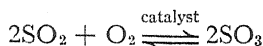
Since the sulfuric acid is strongly ionized it produces only hydrogen and sulfate ions.



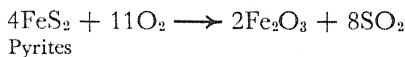
Sulfur dioxide is used as a bleaching agent with reducing action. It reacts with some dyes to remove oxygen from them and form colorless reduced compounds. This is different from the bleaching action of chlorine, which is an oxidizing bleaching agent. Sulfur dioxide is used to bleach straw, wool, and silk. Dried peaches and apricots are treated with sulfur dioxide before they are dried to prevent discoloration. A faint taste of sulfurous acid is detectable in the prepared fruit. Sulfur dioxide was formerly used as a fumigant, but it is seldom used today. Fifty years ago, it was the custom to close the house and burn sulfur candles after someone had had a contagious disease. The sulfur burnt to sulfur dioxide, and it had a mild disinfectant power. Today there are better disinfectants and antiseptics and more is known about contagion. It is no longer considered necessary to disinfect the house after a contagious disease. Sulfites are used as mild antiseptics in some industries. In wine fermentation, undesirable bacteria are removed with very small amounts of sulfite. Sulfur dioxide is also used in large amounts to form sulfur trioxide.

Sulfur trioxide is used for the production of sulfuric acid, one of the heavy chemicals of the United States.

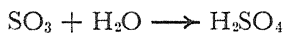
The production of sulfuric acid in the United States in 1948 amounted to 10,950,097 short tons. Most of this sulfuric acid is prepared by the *contact process* which yields a high grade concentrated acid. The *lead chamber process* is responsible for the production of a more dilute acid. The contact process is given this name because the acid anhydride of sulfuric acid, sulfur trioxide, is formed on contact with a catalyst. Sulfur dioxide and an excess of oxygen, usually supplied by forced air, are the reactants. The reaction is reversible, but when it is carried out at 400° C., sufficient sulfur trioxide is produced to make the process economically sound.



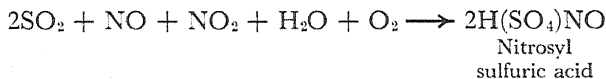
The source of sulfur dioxide may be the burning of sulfur or the roasting of sulfide ores. When, for example, the mineral, pyrites, which contains iron sulfide is roasted, sulfur dioxide is given off as a gas.



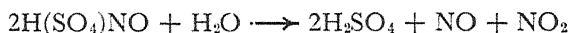
The sulfur trioxide is dissolved in concentrated sulfuric acid, and more water is then added to bring the solution to the proper concentration. Pyrosulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$, is first formed, and on dilution it produces sulfuric acid. The solution is usually diluted to 96% sulfuric acid. The overall reaction is:



The lead chamber process is named for the huge lead-lined towers in which the reaction is carried out. Sulfur dioxide, SO_2 , oxygen, two oxides of nitrogen, NO and NO_2 , and steam react to form nitrosyl sulfuric acid.



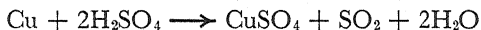
This acid is then hydrolyzed by more steam to form sulfuric acid, and the oxides of nitrogen are released.



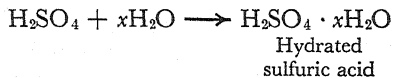
The oxides of nitrogen are reused for the formation of more sulfuric acid. The acid produced by this process has a concentration of 60 to 70 per cent acid, and is not as pure as that produced by the contact process. It is useful in the fertilizer industry, where it is not essential that the sulfuric acid be of high purity.

Sulfuric acid is a dense oily liquid. Concentrated sulfuric acid (96 per cent) has a density of 1.835 grams per milliliter. It is used for the production of sulfates, in the synthesis of other acids such as hydrochloric and nitric acids, many dyes and medicinals, paint pigments, rayon, and in the refining of petroleum. It is used to prepare metal surfaces for galvanizing or enameling, and in the production of a number of metals. In the synthetic fertilizer industry, it is used in the production of ammonium sulfate and of superphosphates.

Concentrated sulfuric acid acts as an oxidizing agent. Metals will react to form sulfates.

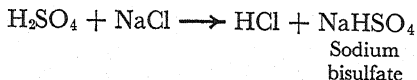


It combines rapidly with water in an exothermic reaction to form a series of hydrates.



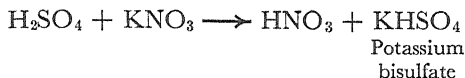
The evolution of heat from this reaction is so great that it is dangerous to add water to the acid. As the drops of water fall into the acid and react, small pockets of steam may be formed and the acid may be sprayed out. The acid must ALWAYS be added to water so that the heat may be absorbed by the total volume of water and so that steam will not be formed in pockets.

Concentrated sulfuric acid will react with the salts of acids which have a lower boiling point to produce those acids. Hydrogen chloride is evolved as a gas when sulfuric acid is poured on chlorides.



A reaction mixture of sulfuric acid and a nitrate must be heated to boil off the nitric acid. Since nitric acid boils at 86° C. while

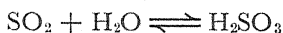
sulfuric acid boils above 270° C., the separation of the two acids is not difficult.



Concentrated sulfuric acid reacts with organic compounds to decompose them. There is usually considerable charring, and an indeterminate number of compounds is formed. Sometimes even carbon dioxide is among the products. Concentrated sulfuric acid produces painful burns on the skin.

Sulfurous Acid

Sulfurous acid is produced from the reaction of sulfur dioxide and water. At 0° C., one volume of water will dissolve 79.8 volumes of the gas, but the solubility decreases as the temperature rises until it is insoluble in boiling water. The reaction is reversible and water solutions of sulfurous acid always have an odor of sulfur dioxide.



It has been pointed out that sulfurous acid is a weak electrolyte and that, therefore, in the solution, there are hydrogen ions, bisulfite ions, and sulfite ions.

PHOSPHORUS

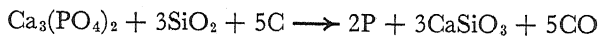
Phosphorus is a member of the nitrogen family and, in many respects, is similar to nitrogen in its chemical properties. Nitrogen is briefly discussed in Chapter 21 on Atmosphere. Phosphorus occurs in nature in a number of minerals as phosphate salts. Phosphate rock is impure calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, usually associated with some calcium carbonate, CaCO_3 . Apatite is a mixed salt of calcium phosphate and calcium fluoride, $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$ with other impurities. Chlorapatite contains calcium phosphate and calcium chloride, $\text{CaCl}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$. Phosphates and carbonates make up the hard matrix of bones and teeth of the vertebrates. Bone ash is an impure calcium phosphate, which is made by removing first the fat and then the

gelatin from bones. The rest of the organic matter is burnt off and the inorganic mixture is left as the "bone ash." Calcium phosphate predominates in the mixture. Bone ash is widely used in fertilizers, in English china, and for the production of phosphorus and phosphates.

The name "phosphorus" was given to the element when it was first prepared because of its phosphorescence. It means literally, "I carry light." If yellow phosphorus is exposed to moist air in the dark, it gives off a faint greenish light. This is the phosphorescence which astounded early chemists in the seventeenth century. The phenomenon is a slow oxidation of phosphorus to phosphorus trioxide, P_4O_6 , with the evolution of energy. (Incidentally, a compound may be truly phosphorescent and have no chemical relation to phosphorus.)

Phosphorus occurs in two allotropic forms, yellow or white phosphorus and red phosphorus. The yellow phosphorus is a waxy cream-colored solid which oxidizes very rapidly in air. It must be stored under water to prevent oxidation. Its kindling temperature is 33°C . and it must, therefore, be handled with forceps. Since body temperature is 37°C ., it may burst into flame if it is held in the hand. Yellow phosphorus is very poisonous, although phosphates are necessary for life. Red phosphorus is a dark red powder with a kindling temperature of 260°C . and it is nonpoisonous. Consequently, it is much easier to handle than yellow phosphorus.

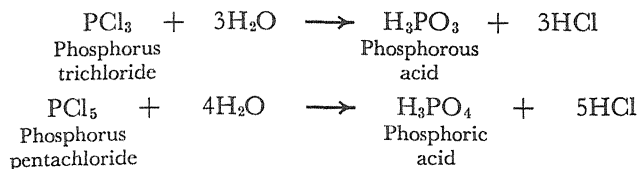
Phosphorus is prepared by heating impure calcium phosphate in an electric furnace with silicon dioxide (sand) and carbon. The carbon reduces the phosphorus to the free element.



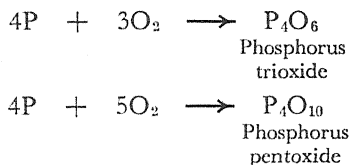
Phosphorus distills off, the carbon monoxide goes off as a gas, and the calcium silicate, CaSiO_3 , forms a slag with the other impurities which can be drawn off from the bottom of the furnace from time to time. The phosphorus is yellow phosphorus, but it can be converted into red phosphorus by heating the yellow form in the absence of air.

Phosphorus forms compounds in which its valence is either three or five. It forms a series of covalent compounds with the halogens. Phosphorus trichloride, PCl_3 , and phosphorus pentachloride, PCl_5 , are examples. These halides are valuable reagents

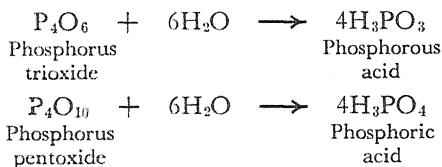
in the synthesis of many organic compounds. They react with water to form acids.



When phosphorus is oxidized in the presence of a limited amount of air, a mixture of two oxides, phosphorus trioxide, P_4O_6 , and phosphorus pentoxide, P_4O_{10} , are formed. With an excess of oxygen, the oxidation yields only phosphorus pentoxide.



These oxides are typical nonmetallic oxides which react with water to form acids. Each forms a series of acids, with the final product the ortho acid. Only these ortho acids will be given.



Salts are formed by both phosphorous and phosphoric acids. The salts of phosphorous acid are called phosphites, whereas those of phosphoric acid are phosphates. The sodium salts are trisodium phosphite, Na_3PO_3 , disodium phosphite, Na_2HPO_3 , monosodium phosphite, NaH_2PO_3 , trisodium phosphate, Na_3PO_4 , disodium phosphate, Na_2PO_4 , and monosodium phosphate, NaH_2PO_4 .

Phosphates are necessary for the life processes of all living things. Thus, fertilizers contain the compounds of at least three elements, nitrogen, potassium, and phosphorus. The analysis on the bag of fertilizer gives the percentage of these three elements. Many fertilizers contain traces of other elements which are also needed for good plant growth.

In your own body phosphates are present as calcium salts in our bones and teeth, and as sodium salts in our blood. There are a large number of organic compounds in your body which are phosphates. There are carbohydrate phosphates, phosphoproteins, and phospholipides. (The lipides are the group of fatty substances among which are the true fats.)

NEW TERMS

Halogen, antichlor, allotropism.

QUESTIONS

1. Explain the formation of chlorine and of sodium hydroxide in an electrolytic cell with a water solution of sodium chloride as the electrolyte. How are chlorine and free sodium formed when molten sodium chloride is electrolyzed?
2. Why is chlorine water a bleaching agent?
3. Which is the stronger oxidizing agent — chlorine, bromine, or iodine? Give one line of evidence to support your answer. Which halogen has the greatest ability to gain electrons?
4. What is bleaching powder? HTH? Why do these compounds act as disinfectants?
5. What is the danger in using bleaching agents in the laundry?
6. How is bromine isolated from sea water? Give reactions.
7. Compare the physical properties of the halogens.
8. Describe the Frasch process for producing sulfur.
9. Why would you describe sulfur as a typical nonmetal?
10. Give three reactions of hydrogen sulfide. How does it ionize?
11. Explain the synthesis of sulfuric acid by both the contact process and the lead chamber process.
12. Why does sulfur dioxide act as a bleaching agent?
13. Write equations for the reactions of sulfurous acid and bases. Name the products. For sulfuric acid and bases.
14. How do the two allotropic forms of phosphorus differ in chemical reactivity?
15. Why is phosphorus essential for the proper nourishment of both plants and animals?
16. Of what acid is phosphorus trioxide the acid anhydride? Phosphorus pentoxide?

The Metals

The metals are a group of elements which, in their free state, have a most important role in the material aspects of daily life. They make up the framework of large buildings and support part of many small houses. They form the pipes which carry water and the basic part of enameled stoves, refrigerators, and bath tubs. They carry current in electric and telephone wires. Most cooking utensils and many of the ornaments of homes are made of metals. Automobiles, trains, airplanes, bridges, farm machinery, and industrial tools are made up wholly or partially of metals. They have been briefly discussed in Chapters 6 and 10.

The metals are elements which have one, two, or three electrons in the outer, or valence, shell of the atom. These electrons are readily lost to other elements to form compounds in which the metal is the positive ion. Physically the metals are solids, with the exception of mercury; most are readily rolled out into sheets (malleability), although some are brittle; some may be drawn into wires (ductility), and all have a luster which is usually silvery. Many are quite dense, although sodium, magnesium, aluminum, and a few more are light. They are good conductors of heat and of electricity.

A few of the metals which are not very active chemically occur free in nature. Gold is a good example. It occurs as tiny flecks mixed with other material, although good-sized nuggets have been found. However, most metals occur as their compounds in complicated mixtures along with other material. The compounds which occur in nature are called *minerals*. They never occur as the chemically pure compound, although one compound will predominate, and the formula which is given for the mineral will be the formula of this compound. If the metal can be economically obtained from the mineral, then the natural material which is frequently rocky but which contains the mineral is called

an *ore* of the metal. Ores which yield relatively large amounts of the metal are called *high grade ore*, while those which yield small amounts of the metal are called *low grade ores*. A process which is widely used for the concentration of ores is the *flotation process*. The ore is finely ground and is whipped up with water, air, and an oil. The water, air, and oil form a froth made up of very fine bubbles. The oil holds the fine particles of mineral in the froth, while the rocky part of the ore, the *gangue*, sinks to the bottom of the water. The ore may thus be separated into a fraction containing a very large percentage of the mineral and one which contains practically none. The process is of great importance economically, since by this one step much of the worthless material in the ore can be discarded.

The reactions by which the free metal is liberated from the mineral differ with the metal and with the chemical nature of the mineral. All the metals must be reduced from the ionic to the free state.

Although metals show a wide range of properties, it is as nothing compared to the scope of properties of the *alloys* of the metals. Alloys are mixtures of metals which are commonly formed by melting one metal and dissolving others in it. They are also formed when two or more metals are electrically deposited at the same time. Many alloys, on hardening, appear to be solid solutions of one metal homogeneously dispersed in the other metal. However, some metals appear to combine when they are mixed, and the alloy may be composed of a solid solution of a compound of the two elements dissolved in one of the metals. A great deal is not known about why metals combine with one another and what kind of compounds they form. A third type of alloy is one in which clumps of molecules of one metal are distributed through the other. The mixture is not homogeneous, but will show a mottled appearance under the microscope. Alloys may be made of just two metals or of as many as three or four metals. Carbon and silicon, nonmetals, are used in a number of steels.

COPPER FAMILY

The copper family occurs as family 1B of the Periodic Table. The members of this triad have similar properties, but they differ quite markedly from the members of family 1A, the alkali

metals. While they form compounds in which the metal has a valence of +1, the most common compounds of copper have a valence of +2, and those of gold have a +3 valence. All three of these elements occur free in nature.

These three elements were the first metals known and used in the ancient world. The fact that all three of them occur free in nature and that copper is readily prepared from some of its minerals accounts for this early knowledge and use. The production of copper tools and ornaments of gold and silver occurred as early as 4000 B.C. in the Near East. Silver and gold, which were rarer than copper, were used for the fabrication of some of the earliest coins. All three elements are mentioned in the Old Testament.

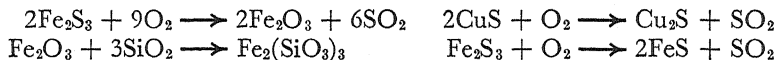
Although some copper occurs free in nature, most of the important copper ores contain compounds of copper. The sulfide ores include chalcocite, Cu_2S , and chalcopyrite, CuFeS_2 , while the basic carbonates are malachite, $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$, and azurite, $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$. The United States is the leading producer of copper ores with large mining centers in Arizona, Montana, Utah, and Michigan. Copper ores are also mined in Chile, Rhodesia, the Belgian Congo, the Soviet Union, Canada, Japan, and Spain.

Silver occurs free in nature, but often as an alloy with other metals. Much of the silver produced in the United States is derived from the anode sludge formed in the refining of copper, since silver is present in small quantities in the copper ores. The principal ores of silver are argentite, Ag_2S , and horn silver, AgCl .

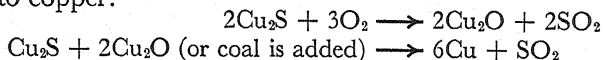
Gold is present in the free state in rock in the veins of quartz. On this continent it occurs in the high and rugged western ranges of mountains. As the rocks weather and form sand and gravel, the flecks of gold are washed down into the stream beds. The "sourdoughs" of the gold rush days "panned" the sand in creek bottoms to find these precious grains. The particles of gold have a much higher density than sand, and when the mixture is shaken in a pan with water, the sand can be washed away and the grains of gold will remain in the bottom. The number of men engaged in this hand operation is now small, but the process of "hydraulic mining" involves the same principle. Sand and gravel banks are washed with a strong jet of water into sluices where the sand and gold are separated.

Copper

The greatest part of the copper produced in the United States comes from sulfide ores. These ores are concentrated by the flotation process if they are low grade ore, the oil is distilled off the foam, and the ore is roasted by heating it in a furnace through which a blast of air pours. The hot sulfides are partially converted to oxide and sulfur dioxide. If the ore contains a large amount of iron oxide, sand is added in order to remove this oxide. The sand combines in the hot furnace with the iron oxides to form a molten, glassy mass called the *slag*, which floats on top. Sometimes calcium oxide (lime) is introduced along with the sand to make slag with a low melting point. The copper is converted to cuprous sulfide, and the iron which has not united with the silicon is reduced to ferrous sulfide.



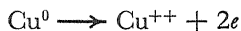
The sulfides collect under the slag and are separated from it by running them off into a converter furnace. This furnace has a series of small openings at the bottom so that a blast of air can be forced through the molten sulfides. The sulfur of the sulfides burns off with the formation of sulfur dioxide; and as cuprous oxide is formed it reacts with more sulfide to form free copper. The charge is also stirred with green wood to reduce the cuprous oxide to copper.



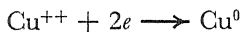
The copper is poured out of the furnaces and allowed to cool. It is called "blister copper" because small bubbles of sulfur dioxide, which are given off as the copper cools, cause the surface to be blistered. This copper is about 99 per cent pure, and it can be used for many articles without further purification. For electric wire, however, a much higher grade of copper is necessary for maximum conductivity of the current.

Pure copper is prepared from the blister copper by electrorefining. Plates of blister copper are used as anodes in an electrolytic cell, while thin sheets of pure copper are used for the cathodes. These are suspended alternately in a bath of copper sulfate, sulfuric acid, and a little chloride. The amount of

electric current flowing through the cell is regulated so that the copper dissolves from the anode,



while silver and gold do not. These metals drop out of the blister copper as it is dissolved to form a finely divided sludge, the anode sludge. At the cathode, copper ions deposit to form free copper:

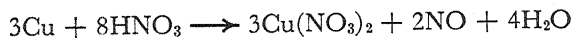


The anode sludge is a rich source of silver, gold, and platinum.

Next to silver, copper has the highest electrical conductivity of any metal. Since copper is much less costly than silver, it is the metal of choice for all electrical wiring. The copper must, however, be very pure copper in order to give efficient conductivity.

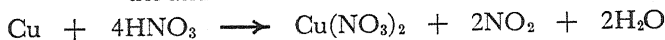
In air at room temperature, copper gradually loses its bright luster, as an oxide film forms. The oxide covers the surface tightly and protects the metal from further oxidation. In moist air, the product is basic copper carbonate, $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$, a bluish green compound that also adheres tightly to the surface. This is commonly called verdigris. Copper is sometimes used for roofs, although it is much more expensive than some other types of roofing — asbestos shingles, for instance. The singular beauty of a copper roof lies in the soft blue-green color of the basic copper carbonate which soon forms over it.

Since copper is below hydrogen in the Electromotive Series, it does not react with nonoxidizing acids, but it is dissolved by acids such as nitric acid or any strongly oxidizing acid.



Dilute ni-
tric acid

Nitric
oxide



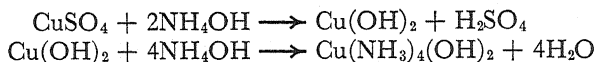
Concentrated
nitric acid

Nitrogen
dioxide

Copper forms a series of cupric salts where copper has a valence of +2. These salts are soluble in water and form bright blue solutions. They are cupric sulfate, CuSO_4 , cupric nitrate, $\text{Cu}(\text{NO}_3)_2$, cupric chloride, CuCl_2 , and cupric acetate, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$. Cupric hydroxide, $\text{Cu}(\text{OH})_2$, cupric phosphate, $\text{Cu}_3(\text{PO}_4)_2$, and cupric sulfide, CuS , are difficultly soluble in water. The cuprous

salts are not as common as the cupric salts. They are difficultly soluble in water. Some of the compounds in which copper has a valence of +1 are cuprous chloride, Cu_2Cl_2 , cuprous sulfide, Cu_2S , cuprous hydroxide, CuOH , and cuprous carbonate, Cu_2CO_3 .

The cupric ion forms a complex ion in which four ammonia molecules are associated with it to form $\text{Cu}(\text{NH}_3)_4^{++}$. Many metals form complex ions which are thought to be held together by coordinate covalence. The pair of electrons belonging to nitrogen, which are unshared in ammonia, are shared with the metal when in the complex forms. This ion, the cupric ammonium ion, is a characteristic deep blue color. The cupric ion may be detected by the formation of this deep blue ion in solutions.



The cuprammonium process for rayon uses a solution of cuprammonium sulfate to dissolve cellulose.

Copper is used extensively in the form of its alloys, the brasses and bronzes. The brasses all contain a large amount of copper with zinc. They are easily machined and have low melting points, but they are not as strong as pure copper. Although they do not rust, they are subject to corrosion. Bronzes are alloys of copper and tin, and sometimes zinc and traces of iron and lead. In general, the bronzes are stronger than pure copper and more resistant to corrosion.

Silver

A great deal of the silver produced in the United States is a byproduct of the refining of copper and lead. The anode sludge formed in the electrorefining of copper is a rich source of silver. Silver and gold in the electrode sludge may be separated either by electrodeposition or by the action of sulfuric acid. Concentrated sulfuric acid will react with silver but not with gold.



If the free metal is desired, it must be produced by the reduction of the silver salt.

Many lead ores contain silver, and when lead minerals are reduced to free lead, free silver is formed at the same time. The

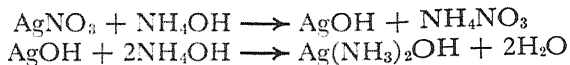
Parkes process is used to separate these two metals. In this process, a small amount of zinc is added to the molten, silver-bearing lead. Zinc readily forms an alloy with silver which has a higher melting point than lead. The alloy of zinc and silver rises to the top of the molten lead and forms a crust which may be skimmed off. The process is repeated until the amount of silver in the lead is extremely low. Any gold in the lead is carried along with the silver zinc alloy. Zinc is separated from the alloy by distilling off the zinc.

Silver is used for coins and, because of its beauty and relative costliness, it is used for jewelry, flatware, and ornaments for the home. In the United States, coin silver is a hard alloy made of 90 per cent silver and 10 per cent copper. Sterling silver contains 7.5 per cent copper. For a discussion of the production of silver plate and the tarnishing of silver, see Chapter 13.

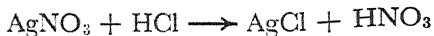
Silver is a fairly stable metal. It does not readily combine with oxygen of the air at ordinary temperatures. It does not react with nonoxidizing acids to release hydrogen, but it is oxidized by nitric acid.



Most silver salts are difficultly soluble in water, with the exception of silver nitrate, AgNO_3 . Many silver salts are colorless solids. Examples are silver chloride, AgCl , silver carbonate, Ag_2CO_3 , silver acetate, $\text{AgC}_2\text{H}_3\text{O}_2$, and silver sulfate, Ag_2SO_4 . Silver oxide, Ag_2O , is brown; silver sulfide, Ag_2S , is black; and silver bromide, AgBr , and silver iodide, AgI , are pale yellow. The silver ion forms a complex ion with ammonia, in which two ammonia molecules are associated with the silver ion.

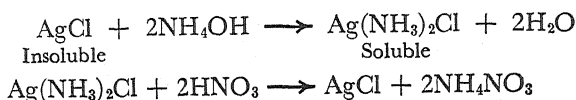


A test for the silver ion is the precipitation of silver chloride, since all chlorides with the exception of mercurous chloride, HgCl , and lead chloride, PbCl_2 , are readily soluble in water. A confirmatory test,



in order to insure that the precipitate is not mercurous chloride or lead chloride, is carried out by dissolving the precipitate in

ammonium hydroxide. Only silver chloride is soluble. It is reprecipitated as the white silver chloride, AgCl , by adding dilute nitric acid.

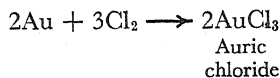


Gold

Gold is a very stable, inactive element. It will not combine with oxygen or react with hydrochloric acid, HCl , sulfuric acid, H_2SO_4 , or nitric acid, HNO_3 . It is soluble in aqua regia, a mixture of nitric acid and hydrochloric acid. Aqua regia ("kingly water") was named by the alchemists since it can dissolve the "royal metal," gold.



Gold combines with chlorine at about 150°C . but not with oxygen.



Gold compounds exist in which gold has a valence of +1 (aurous), but they are not very stable. The common valence of gold is +3 (auric). Examples of gold salts are auric chloride, AuCl_3 , auric bromide, AuBr_3 , auric hydroxide, $\text{Au}(\text{OH})_3$, and auric sulfide, Au_2S_3 .

ALUMINUM

Aluminum is a member of the third group of elements. This group includes twenty-three elements, but all of them are rare except boron and aluminum. Boron is a nonmetal and, although aluminum is amphoteric, its metallic qualities predominate.

Aluminum is widely distributed in nature. It is present in clays of all types as hydrated aluminum silicate, $\text{Al}_2(\text{SiO}_3)_3$, and in shales and slate. Because of this distribution, aluminum is the most common metal and the third most abundant element in the earth's crust. It is not economical, at present, to produce metallic aluminum from clays. The mineral which is the chief

source of aluminum is bauxite, a hydrated aluminum oxide, Al_2O_3 , which is produced in Dutch Guiana, and in the United States in Arkansas and Georgia. Cryolite, Na_3AlF_6 , is another mineral which is essential for the production of aluminum.

In 1886 Charles Hall discovered that aluminum can be reduced to the free metal by electrolyzing a solution of aluminum oxide in molten cryolite. Until his discovery, free aluminum was very rare and very costly. By 1900 aluminum was being produced in the United States in large quantity by this method, and the amount has continued to increase.

The ore, bauxite, is first purified by dissolving it in sodium hydroxide, filtering, and allowing the aluminum oxide to recrystallize. Cryolite, Na_3AlF_6 , is placed in large steel tanks which have a covering of carbon on the bottom to act as the cathode of the cell and which are equipped with carbon anodes which dip into the tank. The carbon anodes are lowered into the tank and, with the current on, an electric arc is produced when the anodes come close to the bottom of the tank. The heat of the arc melts the cryolite. The anodes are raised and aluminum oxide is added to the tank. Free aluminum is formed and collects on the bottom of the tank from which it is drawn off. From time to time, more bauxite is added to the cell. The aluminum which is drawn off is cast into blocks. This aluminum is about 99 per cent pure, but is satisfactory for most uses.

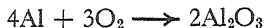
Aluminum has many uses in both industry and the home. The table shows the distribution in 1946.

Distribution of Aluminum Consumption in 1946 *

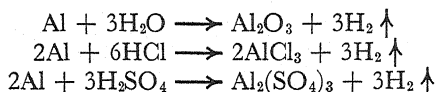
<i>Industry</i>	<i>Per Cent</i>
Aluminum fabricators	25
Building products	18
Transportation	14
Cooking utensils	11
Machinery	6
Household appliances	6
Power transmission	5
Miscellaneous	15

* From "Aluminum," by J. D. Edwards and F. Keller, in Volume I, p. 619, *The Encyclopedia of Chemical Technology*, R. E. Kirk and D. F. Othmer, editors. Copyright, 1947, by The Interscience Encyclopedia, Inc., New York.

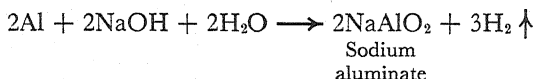
Aluminum is an active metal which combines readily with the oxygen of the air to form aluminum oxide, Al_2O_3 .



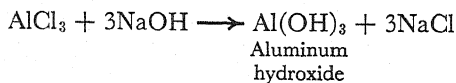
The oxide adheres very tightly to the metal, and as soon as a continuous coat is formed, it prevents the further reaction of the metal. Aluminum reacts readily with hot water to form hydrogen and aluminum oxide, but again the oxide adheres tightly and the action is, therefore, limited. With acids, aluminum reacts vigorously and since the product is a soluble aluminum salt, the action is complete.



Aluminum will also react with either sodium or potassium hydroxide to form hydrogen and a salt in which aluminum is in the negative radical.



The salts of aluminum all show aluminum with a valence of +3. Some of the common ones are aluminum chloride, AlCl_3 , aluminum bromide, AlBr_3 , aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, and aluminum silicate, $\text{Al}_2(\text{SiO}_3)_3$. All are colorless. The soluble salts of aluminum react with bases to form a white gelatinous precipitate of aluminum hydroxide, $\text{Al}(\text{OH})_3$.



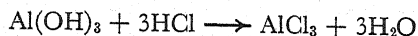
If an excess of the base is added, the aluminum hydroxide dissolves with the formation of an aluminate.



In other words, aluminum hydroxide acts as if it were an acid, H_3AlO_3 or HAlO_2 , and the above equation might be written:



Aluminum hydroxide also acts as a typical base when it reacts with acids.



Since aluminum hydroxide reacts with both acids and bases, it is amphoteric but the nonmetal properties of aluminum are not as pronounced as the metallic ones.

Aluminum sulfate forms double salts with other sulfates which readily crystallize from water into large perfect crystals. These double salts are called *alums* and crystallize as hydrates. Examples are potassium alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, sodium alum, $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$.

IRON

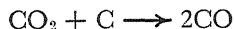
Although all the metals which are being studied are important in daily life, more iron is used in the fabrication of the things you use, than any other metal. It is frequently used in the form of its alloys which have a much wider range of properties than pure iron.

There are large deposits of hematite, Fe_2O_3 , in the Lake Superior region in Minnesota, Michigan, and Wisconsin, which supply a major portion of the iron produced in this country. The ore is loaded on very large lake ships and taken by water route to the smelting centers of the country. Some magnetite, Fe_3O_4 , and some limonite, Fe_2O_3 , are used but in much smaller quantities than hematite.

Hematite is a high grade ore which is readily reduced in a blast furnace to free iron. The furnace is charged with the ore, coke, and limestone, and in case the ore is low in sand, some of that is added to form a good slag. Hot air is blown into the bottom of the tall blast furnace. The coke at the bottom of the furnace burns fiercely to produce a hot medium for the reaction.



As the hot carbon dioxide is swept up the furnace, it reacts with more carbon to produce carbon monoxide.



Carbon monoxide reduces the ferric oxide to free iron.

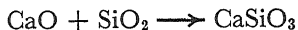


The molten iron trickles down to the bottom of the furnace. Slag floats on top of the iron and protects it from oxidation at

the high temperature of the furnace. The slag, a molten glass, is formed when limestone decomposes to form calcium oxide



which reacts with silicon dioxide, the sand.



This molten glass carries down the impurities in the ore. Both liquid slag and liquid iron are periodically drawn off from the furnace. The furnace operates continuously. New charges of ore, limestone, and coke are added from time to time through the top of the furnace. Not all of the carbon monoxide produced is used in the reduction of the ferric oxide. The gases issuing from the top of the furnace, which contain the excess carbon monoxide, are therefore burned to supply energy to heat the air blown in through the bottom of the furnace. The slag is used for the production of the insulating material known as *mineral wool*, as well as for filler in concrete work and cement blocks.

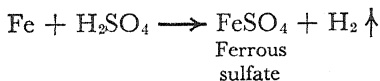
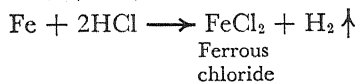
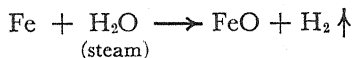
The iron which is produced from the blast furnace contains several per cent of carbon, about the same concentration of silicon and small impurities of other elements. It is called *pig iron*, since it was formerly cast in molds which were called pigs. The pig iron has a low melting point compared to other iron alloys. But it also has a low tensile strength and is quite brittle. It is therefore worked, and the composition is changed before it is fabricated into articles.

Cast iron is made by adding scrap iron to the pig iron and pouring the alloy into molds. It has better tensile strength than pig iron, but cannot stand sudden shocks or blows and cannot be welded. It is molded into objects such as radiators, window sash weights, stoves, the base for bath tubs, and other things that do not require great strength.

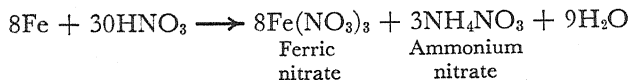
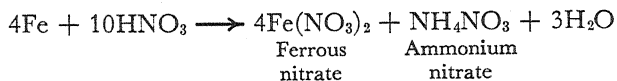
Wrought iron is made from pig iron by removing the impurities by oxidation. Various methods are used, but one method is to blow very hot air through the molten iron. Carbon, sulfur, and phosphorus are oxidized to oxides which are blown off in the stream of air. Silicon and manganese form oxides which unite with the furnace walls to form a slag. Wrought iron is almost 99 per cent pure and has a fibrous quality and strength which make it useful for nails, bolts, nuts, pipes, rails, and many other objects.

Most iron goes into the formation of *steel*. Steels are a series of alloys of iron and carbon in which the carbon content varies from a few hundredths of a per cent up to several per cent. Often other elements are added to yield steels with special properties. Stainless steel contains 15 per cent chromium and is remarkably resistant to corrosion; manganese steel contains 10 to 18 per cent manganese and is extremely hard and durable; tungsten steel which contains 10 to 20 per cent tungsten is hard at high temperatures. These are three examples of steels with very different properties and, therefore, different uses.

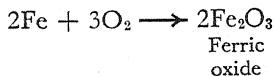
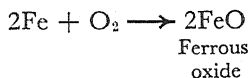
Chemically pure iron is a fairly active metal. It will react with steam to release hydrogen and with acids.

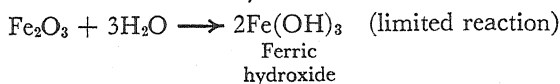
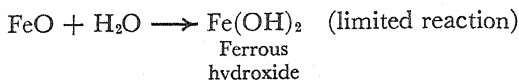


With cold dilute nitric acid, no hydrogen is evolved, but ammonium nitrate is formed. If the acid is very dilute, the iron forms ferrous nitrate, while with more concentrated acid, ferric nitrate is the product. Iron does not react with concentrated nitric acid.

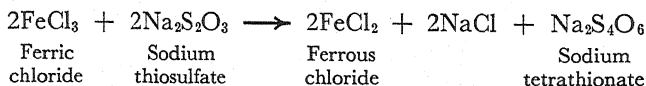
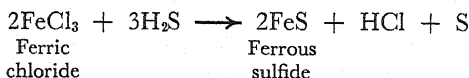
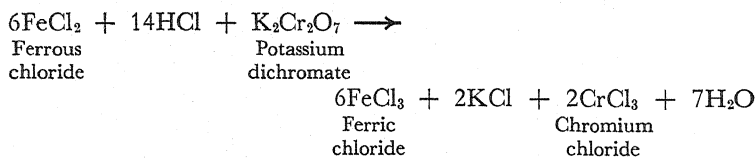
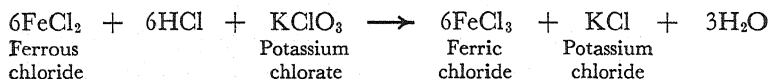


Iron rusts rapidly in moist air to produce a mixture of compounds. They appear to be ferrous and ferric oxides and hydroxides. Carbon dioxide in the atmosphere reacts with these compounds to form carbonates.





Iron forms a series of compounds in which the valence of the iron is +2 and another series in which the valence is +3. The first series of compounds is called *ferrous* while the other series is named *ferric*. This follows the rule of naming compounds of elements with variable valence in that the higher valence is called “-ic” while the lower valence is called “-ous.” Ferrous compounds are green or brown-green in color, while ferric compounds are yellow to red-brown. Common salts are ferrous chloride, FeCl_2 , ferrous sulfate, FeSO_4 , ferrous nitrate, $\text{Fe(NO}_3)_2$, and ferric chloride, FeCl_3 , ferric sulfate, $\text{Fe}_2(\text{SO}_4)_3$, and ferric nitrate, $\text{Fe(NO}_3)_3$. Ferrous salts are converted into ferric salts by mild oxidizing agents such as nitric acid, HNO_3 , potassium permanganate, KMnO_4 , potassium chlorate, KClO_3 , and potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$. Ferric salts are reduced to ferrous salts by such reducing agents as hydrogen sulfide, H_2S , sulfurous acid, H_2SO_3 , and sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$.



NEW TERMS

Mineral, ore, flotation process, alloy, complex ion, metallurgy, alums.

QUESTIONS

1. Describe the metallurgy of copper. How is pure copper produced from blister copper?
2. Why is copper soluble in nitric acid but not in hydrochloric acid?
3. Give the formulas for a series of cuprous salts. What are the corresponding cupric salts? Which are most common?
4. What is a test for the cupric ion? What is the cuprammonium ion?
5. What is the valence of the silver ion? Does it show more than one valence?
6. What are the valences of gold? Give examples of specific salts.
7. Why is aluminum called an amphoteric element? Do its metallic or nonmetallic properties predominate? Explain.
8. How is aluminum produced from bauxite?
9. Is aluminum an active metal? Why is it possible to boil water in aluminum without excessive solution of the metal?
10. Would it be possible to boil a solution of a base in an aluminum pan? An acid? Why?
11. Explain the production of pig iron. For what is it used? What is wrought iron? How does it differ from pig iron?
12. What is the difference between ferrous salts and ferric salts? Give one method for converting ferrous chloride to ferric chloride. Give one method for converting ferric chloride to ferrous chloride.

Glass and Pottery

Articles of pottery and glass have been used in the households of man for centuries. Archeological exploration has revealed the presence of pottery fragments in prehistoric remains widely distributed. Probably many groups of primitive men recognized the usefulness of sun-dried clay for bowls and vessels. Later it was discovered that fire improves the quality of these articles, and pottery was crudely fired. Natural glass, obsidian, was worked into arrowheads, knives, and razors, but for ages no glass was made by man and no glaze applied to pottery. Phillips (*Glass: The Miracle Maker*) quotes Petrie, "The earliest known

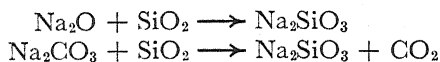
glaze is that on stone beads of The Badarian age in Egypt about 12,000 B.C. This is green. The oldest pure glass is a moulded amulet of deep lapis lazuli color, of about 7000 B.C." It was not until man was quite civilized that he began to make glass objects and his knowledge of methods was probably discovered accidentally.



Fig. 20-1. Ancient glass vase, Egyptian, XVIII dynasty, 1380-1350 B.C. (Courtesy of the Metropolitan Museum of Art.)

Silicon

Chemically, glass and pottery are mixtures, primarily of silicates and silicon dioxide. Although silicon, itself, appears metallic, most of its chemical properties are those of a nonmetal and the common compounds contain the silicon in the negative radical. The silicic acids, H_2SiO_3 and H_4SiO_4 , the common acids of silicon, react with bases to form salts. It is the second most common element in the earth's crust, occurring to the extent of 27.7%. Rocks, sand, clays, and soils are made up of silicon dioxide, SiO_2 , and the silicates and since these earthy materials vary in their composition and appear to be mixtures, it is common to write their composition as oxides, i.e., $\text{Al}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot 6\text{SiO}_2$. This particular mixture, a feldspar, contains some aluminum silicate, some potassium silicate and some silicon dioxide. Silicon dioxide will react at elevated temperatures with metallic oxides or with compounds which yield metallic oxides to form silicates.



Sodium and potassium silicates readily melt and dissolve SiO_2 and other silicates. When the resultant liquids are slowly cooled, the viscosity increases until the liquid is practically rigid, although crystallization does not occur. This is a glass. A *glass* is a supercooled liquid in which there is a random arrangement of molecules rather than the ordered one of crystals. Occasionally glass will crystallize on standing, but all precautions are usually taken to

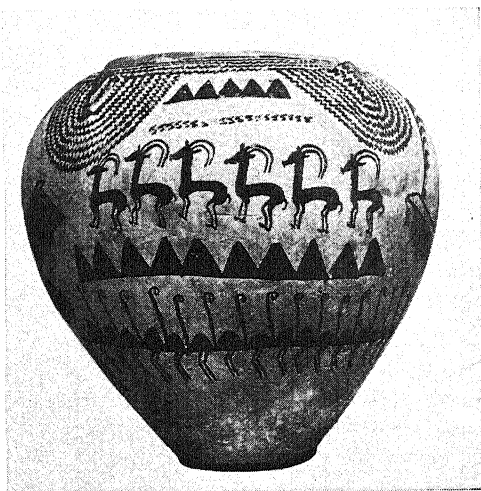


Fig. 20-2. Ancient pottery vase, Egyptian, predynastic. (Courtesy of the Metropolitan Museum of Art.)

prevent it. Crystallized glass is of little value since it loses its transparency and is very brittle.

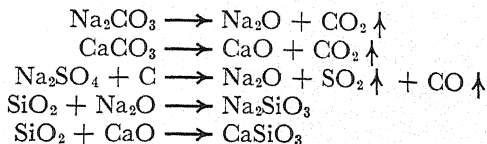
GLASS

Economically one of the most important types of glass in the United States is soda-lime glass. From it window glass, tableware, and containers are made with an estimated value of that produced in 1939 of \$266,617,000. This is glass composed principally of the low-melting silicates, Na_2SiO_3 , and CaSiO_3 , and SiO_2 . Since pure chemicals are not used, other silicates such as ferric silicate, aluminum silicate, and magnesium silicate will be present in small amounts. Frequently small amounts of decolorizers are added to conceal the color imparted by iron salts, a common contaminant of sand (green and yellow bottle glass have an appreciable quantity of iron salts.) The quantity of sodium oxide (Na_2O , as it is reported) and calcium oxide, lime, CaO , must be carefully regulated. A high level of sodium oxide renders the glass too water soluble while a low level of Na_2O and high CaO introduces a tendency toward crystallization.

The production of glass consists of two stages: (1) the preparation of the melt and (2) the fabrication of the glass. Crude materials are placed in pots and heated to 14–1500° C. A typical mix for a soda lime glass is the following:

Sand (SiO_2)	100 parts
Soda ash (Na_2CO_3)	30
Limestone (CaCO_3)	16
Salt cake (Na_2SO_4)	12
White arsenic (As_2O_3)	0.5
Cannel coal (C)	0.5

Many of the reactions which occur produce gases which bubble through the mix and aid in stirring and producing homogeneity. The carbonates decompose to oxides and CO_2 ; the sulfates are reduced and yield SO_2 , CO , and oxides.



The oxides react with SiO_2 to produce fusible silicates which then dissolve more SiO_2 . Frequently scrap glass (cullet) is added to the pot to hasten solution.

Lead-potassium glass is a glass containing lead and potassium silicates in place of the sodium and calcium silicates of soda-lime glass. It may be made in a wide range of refractive indices for high grade lenses, etc. A very heavy lead-potassium glass with a high refraction is used for high quality tableware. It is called *flint glass* or *rock crystal* because of its sparkle and brilliance and the ease with which it is cut.

<i>Lead-Potassium</i>	<i>Glass Mix</i>
SiO_2	100
Pb_3O_4	66
K_2CO_3	38
KNO_3	13
As_2O_3	1

Lead-potassium glass is therefore a mixture of silicon dioxide dissolved in lead silicate and potassium silicate.

Many of you are now familiar in your homes with heat-shock-resistant glasses such as Pyrex and Flameware. These glasses contain borosilicates and are of great usefulness because of their small coefficient of expansion on heating, their excellent chemical stability, their resistance to

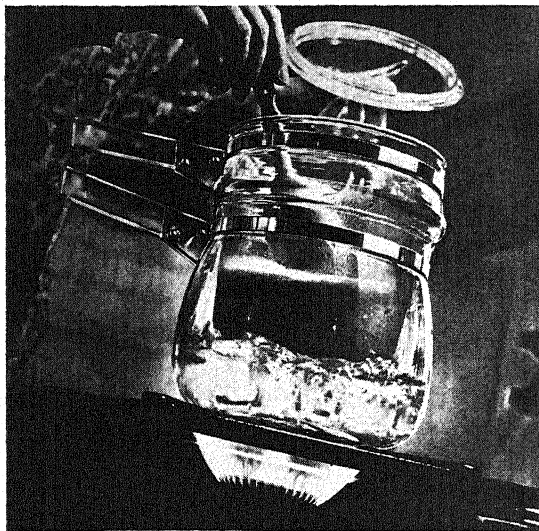
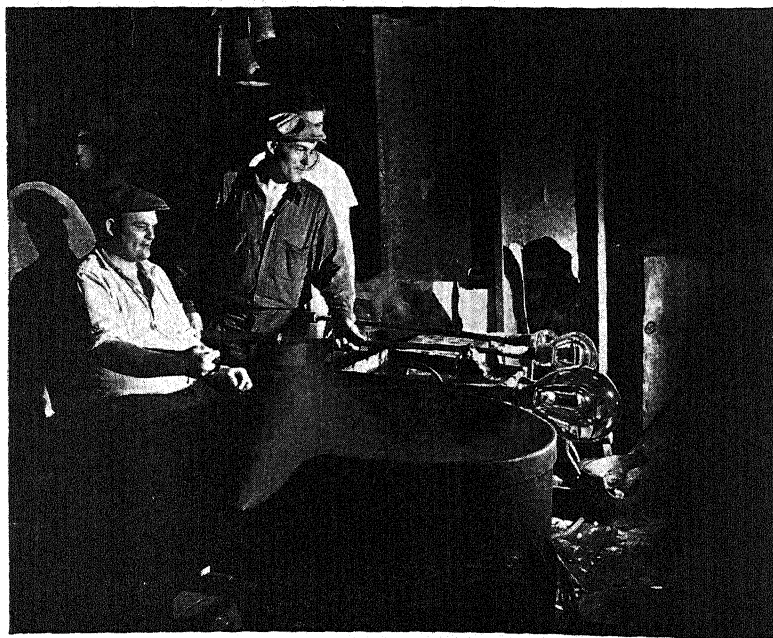


Fig. 20-3. A borosilicate glass shows great resistance to heat shock because it has a low coefficient of expansion. (Courtesy of Corning Glass Works.)



Fig. 20-4. The "gatherer" removes an accurate amount of glass from the furnace on the end of the blow iron. How he rolls the glass on the end of the iron and the amount determines the quality of the finished piece. (Courtesy of Corning Glass Works.)

Fig. 20-5. The "gatherer" blows the glass into a ball and then turns it over to the "ball holder," who rolls and shapes it. (Courtesy of Corning Glass Works.)



crystallization, and their durability to mechanical shock. These glasses are used for baking dishes, pans, electric insulators, laboratory equipment, piping, etc. A typical borosilicate glass has the following composition:

SiO_2	80.5
B_2O_3	12.9
Na_2O	3.8
K_2O	0.4
Al_2O_3	2.2

Some laboratory ware and some window glass have been made of pure SiO_2 . This is called "silica glass," "vitreous silica," or "quartz glass," and is difficult to prepare. The silicon dioxide melts at 1710°C ., and in the liquid state is very reactive chemically. It also contains small bubbles of air which are difficult to remove, even in a vacuum. In many laboratory articles of silica glass, the bubbles are clearly visible. These difficulties in handling make silica glass expensive. It does, however, have some qualities which make it a valuable glass. It has great chemical resistance, high melting point, a very small coefficient of expansion and excellent electrical

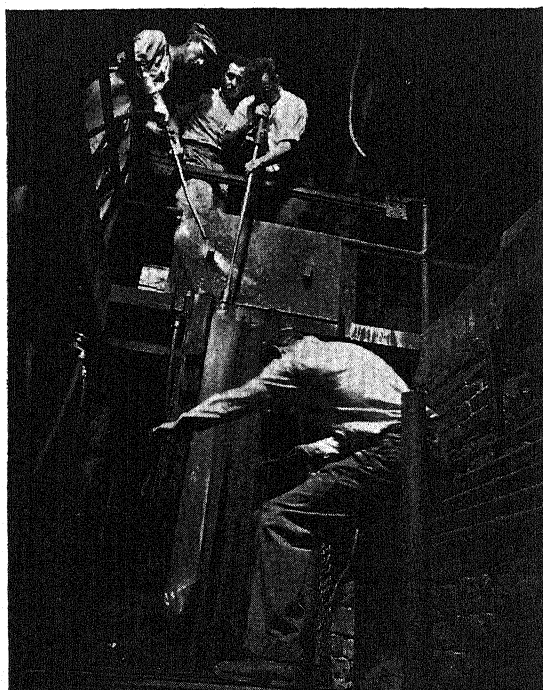


Fig. 20-6. Finally the "gaffer" blows and shapes the hot glass. Here the "gaffer" blows the glass into a mold. (Courtesy of Corning Glass Works.)

resistance. It is able to transmit ultraviolet light and is valuable from this standpoint.

For many centuries, the principal method of fabricating glass articles was by blowing, and it is still used for expensive glassware today. The glassblower has a long pipe with a small bulb at the end on which he "gathers" glass while it is hot but viscous enough to handle. With great skill he blows spheres and cylinders for the production of all sorts of hollow ware. Sometimes the glass may be blown into a mold to get an intricate shape. Today much of the cheap glass is blown by a machine, although the same general methods are used. The machine gathers a definite quantity of glass, air pressure begins to produce a bubble, a mold is placed around this, the bottle is formed, cooled, annealed, and removed — the whole process completely mechanical. Some glass may be stamped.

Annealing is a process for removing strains in glass and rendering it more durable. When glass with an appreciable coefficient of expansion is cooled, the rate of cooling on the outside is much more rapid than the inside and strains develop which make the glass susceptible to shattering. Glass is an-

nealed to relieve the strains by passing it through a warming oven in a continual process. The glass is softened sufficiently to remove the strains and then quickly cooled.

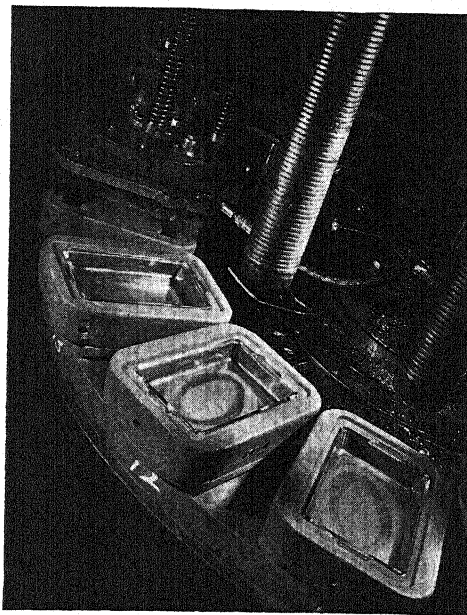


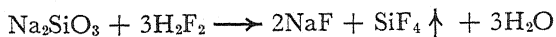
Fig. 20-7. Stamping cake dishes. The gob of glass falls into a mold and is automatically stamped into shape. (Courtesy of Corning Glass Works.)

Colored Glass

Color occurs in glass when some wavelength is absorbed as the light passes through the glass. Thus the glass appears green when red is absorbed. Color in glass may be produced by the formation of a silicate which absorbs light or by the production of particles of colloidal size. An example of the first type is the yellow glass produced when nickel oxide is added to borosilicate glass. The chemical composition of the glass is also important in the color which develops. The influence of the glass is seen in the fact that nickel oxide in soda-lime glass is brownish yellow, in lead glass it is purple. When the color depends on a colloidal particle, the shade and color vary with the size of the particle rather than its nature. Thus ruby glass has for centuries been prepared by dissolving gold in glass, cooling and then reheating until the color "strikes" as colloidal particles form. Copper ruby glass may be formed in the same fashion. If the glass is overheated, the particles are larger and the color is violet to blue.

Yellow	Se or UO_3	to soda-lime glass
Blue	CoO	to soda-lime glass
Greenish blue	CuO	to soda-lime glass
Green	Cr_2O_3	to soda-lime glass

Decorations are added to glass by sandblasting, etching, chipping, or grinding. Sandblasting is used in producing translucent window glass and in decorating ovenware. The pattern is produced by the use of a stencil. In etching, the glass surface is covered with wax, paraffin, or rosin; the design is scratched on, and the glass is treated with hydrofluoric acid. The silicates react to form soluble or volatile products.



Cutting is achieved by the use of an abrasive wheel of sandstone or Carborundum which grinds off the glass. In recent years beautiful art glass has been produced by "copper wheel engraving," a special method of cutting. A shallow intaglio is produced which appears like bas relief, the design sharp, clear, and three dimensional.



Fig. 20-8. Etching. A graduated cylinder is calibrated by scratching through a wax coating and then inserting it in a bath of hydrofluoric acid. (Courtesy of Corning Glass Works.)

Vitreous Enamelware

Enamelware is used in the home in enameled pots and pans, stoves, refrigerators, bath tubs, and sinks. The pots and pans are sheet steel covered with a glass, a vitreous enamel, while tubs and sinks are cast iron covered with the glass. In order that the object may be durable to heat changes, it is necessary that the coefficient of expansion of the glass and the metal be approximately equal. The glass may have oxides added to color it and usually has some infusible oxides added to make it opaque (SnO , SnO_2 , $\text{Ca}_3(\text{PO}_4)_2$, CaF_2 or clay).

The enamel is prepared as a glass, fritted, ground, and dried. It is dusted on the red hot vessel and heated in an oven until it melts. This process is usually repeated three times to build up a glassy layer. The article then has the properties of glass plus the strength of the metal body. Many enamels are low-melting glasses, high in sodium silicate and are not very resistant to acid. Acid-resistant enamels are frequently borosilicates and are available in household equipment. Refrigerators are almost always lined with vitreous enamel (sometimes called porcelain) since it is not readily stained by food and does not have an odor. Most are covered on the outside with an organic enamel not a glass.

In using enamelware the fact that the enamel is a glass must be considered. Although the tensile strength of the ware is quite good since the metal reinforces it, the ware will chip and crack

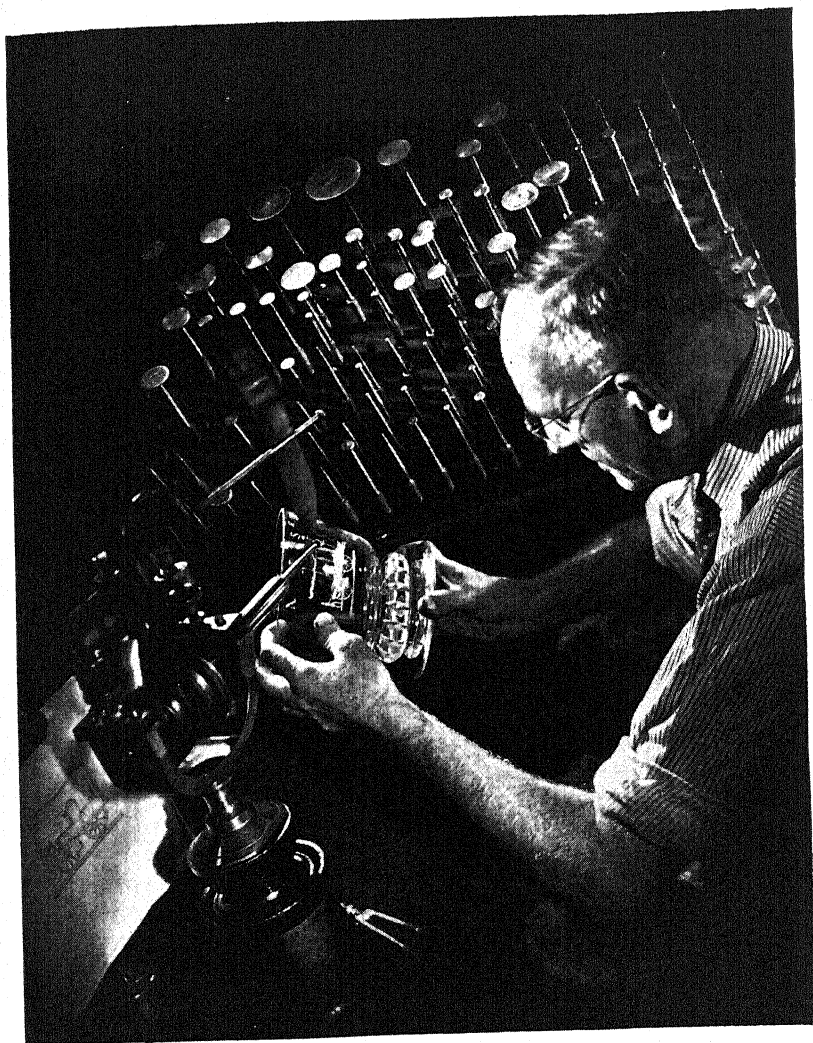
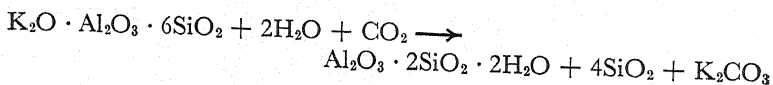


Fig. 20-9. Copper wheel engraving. The bowl is held against a rotating copper wheel which cuts through the glass. This is handwork and requires great skill. (Courtesy of Corning Glass Works.)

when subjected to blows or sharp temperature changes. The poor resistance of much vitreous enamel to acid makes it unwise to allow acid foods such as tomatoes to stand for extended periods in the ware.

CLAYS AND POTTERY

Clays which are found widely distributed over the earth, are produced by the weathering of minerals such as the feldspars, molecular mixtures of hydrated potassium (or sodium) and aluminum silicates. As rain and surface water containing dilute H_2CO_3 trickle over the feldspar, soluble K_2CO_3 forms and is dissolved away, leaving the aluminum silicate-silicon dioxide mixture.



A number of aluminum silicates occur in nature, some valuable for firing, others not. Clays appear to be mixtures of these compounds. *Primary clay* is the residue from weathering of rock in the original place.

When it is uncontaminated by iron salts, it is white, fires white, and is called *kaolin* or *china clay*. Clay which has been moved by geologic disturbances such as glaciers, from the site of formation is

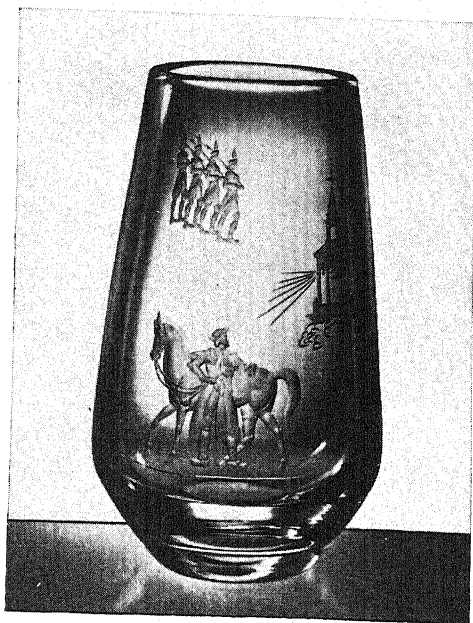


Fig. 20-10. A Steuben vase of great beauty. The Paul Revere vase by Sidney Waugh. (Courtesy of Corning Glass Works.)

frequently mixed with sand, small rocks, and organic material. It is called *ball clay* and usually must be purified before use.

In using clays the physical properties are of utmost importance. When a clay hydrates, it becomes plastic. By plastic, it is meant that the clay may be molded. If you take a ball of hydrated clay and squeeze it, it readily assumes the print of your hand and when it is released retains this print. This is the property of plasticity. The plasticity of the clay varies with the chemical composition and the size of the colloidal particles of clay.

If the clay is composed only of aluminum silicates which have a high melting point, on heating it will dehydrate, shrink, become covered with cracks, and ultimately crumble. If there are residues of feldspars containing potassium or sodium silicates in the clay, these compounds will fuse as the article is heated and flux (dissolve) some of the SiO_2 and aluminum silicate. If the quantity of sodium or potassium silicate is high in the clay, an article will soften and lose its shape on firing. A valuable clay is one which has sufficient fusible silicates to knit the whole together, but a small enough amount so that the clay article does not soften and collapse on firing as they fuse. On cooling the article will be hard and durable and almost impervious to water or oil solutions. It will be made up of a glass with many small particles of nonfusible material dispersed through it. The article has been *vittrified* by firing. *Vitrification is the process of becoming glassy*. Most artists and manufacturers blend clays so that correct plasticity and a desirable balance of fusible and nonfusible silicates are obtained.

Clay is prepared for molding by first crushing and screening to free it from pebbles, twigs, etc., and then colloiddally dispersed by grinding and adding alkali. The noncolloidal material separates by sedimentation and the colloidal clay is then coagulated by adding acid. To this clay, feldspar and sand are added so that the composition of the resultant mix is balanced as to fusible and nonfusible silicates. Enough water may be added to prepare either a thick paste or a thin dispersion about the consistency of cream, called "slip." These are aged so that hydration and thereby plasticity may increase.

The slip is used by pouring it into a plaster of paris mold, porous enough so that much of the water is absorbed. When a

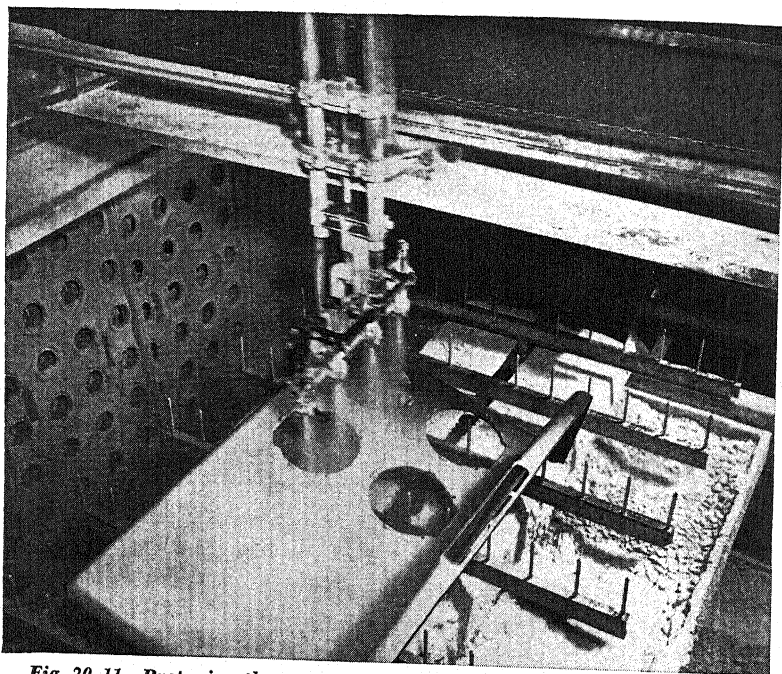


Fig. 20-11. Preparing the top of a stove for the oven. A very finely powdered glass suspended in water is automatically sprayed over the metal. At oven temperatures the glass melts and forms a continuous surface. This stove top will be thin as possible and yet still resistant to wear. (Courtesy of Kalamazoo Stove and Furnace Company.)

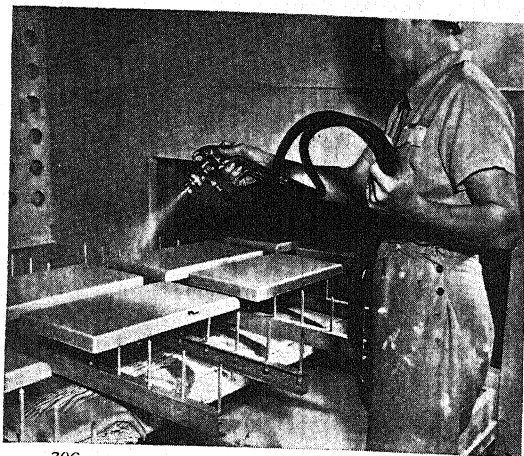


Fig. 20-12. Hand-spraying fritted glass on parts of a stove. (Courtesy of Kalamazoo Stove and Furnace Company.)

sufficient cake of clay has built up, the excess slip is poured out and the remainder allowed to dry. It shrinks on drying and is readily removed from the mold.

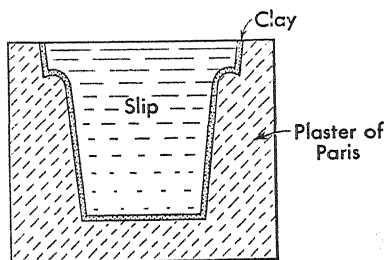


Fig. 20-13. Diagram of a slip mold. Slip is poured into the plaster of paris mold and allowed to stand. Water is absorbed from the slip and a layer of clay is deposited.

The paste may be shaped on a potter's wheel, on a revolving table, by hand, or with a pattern, or if the shape is simple, such as a bowl or saucer, it may be *jiggered*. In jiggering, the clay is pressed down into a rotating mold, by means of a former. The bottom of the article is molded while the top is shaped.

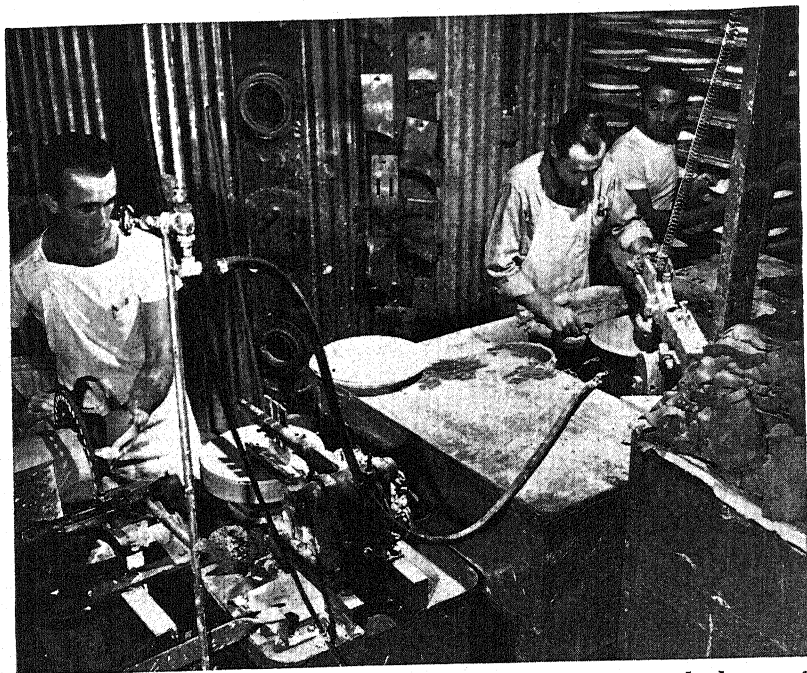


Fig. 20-14. Jiggering plates. The man on left is cutting off a standard amount of clay; the man in the middle is jiggering the plate; and the man on the right is stacking the plates for the kiln. (Courtesy of Gladding, McBean & Company.)

Whiteware is the general term in the ceramic industry for chinaware, earthenware, porcelain, stoneware, and vitreous ware. All these are clay products with varying amounts of fusible silicates, fired at moderately high temperatures (1200 to 1500° C.). Since the amount of vitrification varies with the amount of (1) fusible silicates capable of formation, (2) the temperature of firing, and (3) the time of heating, these products will vary in vitrification from earthenware to porcelain. These wares are classified according to the following rather broad categories: *

Earthenware is a porous, nontranslucent ware with a soft glaze. It is sometimes called semivitreous dinnerware.

Chinaware is vitrified translucent ware with a medium glaze which resists scratching to a greater or less degree.

Porcelain is thoroughly vitrified translucent ware which resists scratching to a maximum degree. This includes chemical and insulation porcelain.

Stoneware usually has a high degree of vitrification but is made of crude materials and is not as carefully handled. Examples of it are found in crocks and bean pots in the home.

Glazing

Since clay products after firing are not completely impervious to water or to scratching, they are covered with a thin layer of

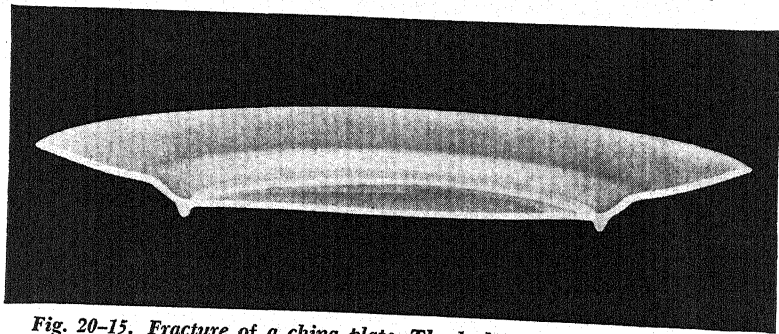


Fig. 20-15. Fracture of a china plate. The body of the plate is smooth and well vitrified while the glaze has sunk into the body. The fracture appears continuous from glaze through body through glaze. (Courtesy of Gladding, McBean & Company.)

* From Watt, *The Selection of Dinnerware for the Home*, Expt. Station Circ. 21, Third Edition. Ohio State University.

glass, the *glaze*. It is common to fire the clay to produce an unglazed "biscuit" and then to add the glaze and fire the article again. If the temperature of vitrification of the glaze is lower than that of the biscuit, the object will consist of a porous body covered by a thin layer of glass. This is typical of earthenware, and in a fragment two distinct layers can be distinguished. If the temperatures of vitrification of the glaze and biscuit are not far apart, the glaze sinks into the body and there is no sharp line of demarcation between body and glaze. This is true in porcelain. A cross section shows a progressive change in extent of vitrification between the body and glaze.

The coefficient of expansion of the glaze compared to the body is of importance in the durability and usefulness of the ware. When there is excessive contraction of the glaze, "crazing" occurs, the glaze is covered with fine cracks, and water solutions and fats begin to soak into the body and discolor it.

The process of glazing may be accomplished by the simple device of throwing salt into the kiln, "salt glazing." Fusible sodium silicate is produced, and a sodium aluminum silicate glaze is formed. This type of glazing is difficult to control, however, and is usually only used on rough articles, such as bean pots and crocks. The glaze is very glassy and is sometimes pitted and irregular.

Where glazing is done carefully, a suitable glass is prepared, ground, and suspended in water. It is then applied by dipping, brushing, or spraying. On heating, the glass melts and forms a continuous glaze. If the melting point of the glaze is high, and the temperature of the kiln is likewise high, the glaze sinks into the body and forms chinaware or porcelain. If it is a low-melting glaze, it merely forms a thin layer over the body.

Color decoration of the ware is applied by one of two methods, underglazing or overglazing. In underglazing, the glaze (colored glass) is painted on the biscuit, fired, and then covered by a transparent glaze. In overglazing, oxides are painted on the glaze and in firing, develop into colored silicates. The chemistry of the changes in color which occur on firing are fairly well understood for those glazes used commercially. However, many ceramic artists use glazes whose composition is not completely known and whose development is therefore incompletely understood. The artist sometimes uses ashes of plant materials which



Fig. 20-16. Dip-glazing cups. (Courtesy of Gladding, McBean & Company.)

may vary in composition. In the kiln the ware is fired either in a reducing or an oxidizing flame and the nature of the glaze produced, and its color and patina, are thereby controlled. For example in a reducing flame, metallic oxides may be reduced to metal and the glaze will be grayed or even black, depending on the extent of reduction. An overglaze may be readily recognized because it is raised above the rest of the glaze. With an underglaze, the decorated surface is absolutely smooth and uniform. Decoration may be achieved in many other ways. Sometimes slip with a high percentage of fusible silicates is used as the glaze. Articles are decorated by incising designs, by applying medallions, and in a great variety of other fashions.

NEW TERMS

Soda-lime glass, lead-potassium glass, flint glass, rock crystal, borosilicate glass, annealing, primary clay, kaolin, china clay, ball clay, vitrification, slip, jiggering, whiteware, earthenware, chinaware, porcelain, biscuit, glaze, crazing, overglaze, underglaze.

QUESTIONS

1. What chemical reactions occur when glass is made?
2. Why are cheap articles made of soda-lime glass? What are the disadvantages of this glass?
3. What are the advantages of lead-potassium glass?
4. Borosilicate glass has a low coefficient of expansion. Why is this important in ovenware?
5. Give three methods of applying designs to glass.
6. What are the two types of colored glass? How are they made?
7. How is glass blown?
8. What is the difference between kaolin and ball clay? How can we account for this difference?
9. How is clay prepared for use in pottery articles?
10. What is slip? How is it used?
11. How are articles jiggered? What type of articles are suitable for jiggering?
12. What are the differences in properties between earthenware, china-ware, porcelain, and stoneware?
13. What is crazing? Why does it occur? What are the disadvantages?
14. How are pottery articles glazed? What is the use of the glaze?
15. How can you distinguish earthenware from chinaware?
16. How can you distinguish an underglaze from an overglaze?
17. How is enamelware produced? What is the difference in function between a glass and an organic enamel? What are the advantages and disadvantages of enamelware?

The Atmosphere

The atmosphere is the gaseous envelop which surrounds the world. This word means the gaseous envelop which surrounds any body whether it is a large planet like the world or a small body. The atmosphere of the world is called "the air." It is composed of a mixture of gases which is at its densest at sea level. The envelop appears to thin out as you travel out in space. Mountain tops stick up into a gaseous mixture which is less dense than that at sea level.

It has been shown that the atmosphere is a mixture rather than a compound by applying the criteria used to differentiate these two types of matter in Chapter 2. (1) The properties of the atmosphere are the sum of the properties of the various elements and few compounds of which it is composed. The color, the pressure, the density, and the odor are all the sum of the properties of these components. (2) The air can be separated into different substances by physical means. If dry air is cooled and compressed, it changes into a liquid. When this liquid air is slowly warmed, some of the rare gases and nitrogen boil off leaving a mixture which becomes richer and richer in oxygen. If air were a compound, all the components would boil off at the same time at the same temperature. (3) When the components which make up the air are mixed together, energy is neither released nor

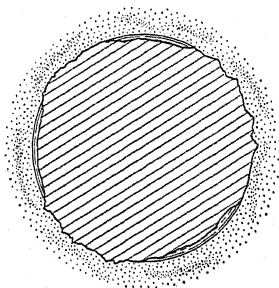


Fig. 21-1. The earth and its gaseous envelop, the atmosphere.

used up. This indicates that no chemical reaction has taken place and that no compound is formed. (4) Air has been analyzed all over the world and these many samples have a variable composition. The variation is not great for most of the components other than water, but if the air were a compound there would be no variation at all. So it is concluded that, by all the tests, air is a mixture.

COMPOSITION OF AIR

Air is composed of nitrogen, oxygen, carbon dioxide, the rare gases, and water vapor. Nitrogen is the chief element present with oxygen next. Together, these two elements comprise about 99 per cent of the air. The other substances make up the remaining 1 per cent. The relatively constant composition of the air is due to the movement of the air as it flows from regions of high pressure to those of low and as it is warmed and rises or cooled and falls. You might think that the air of the city where thousands of furnaces and engines are using up oxygen and where thousands of people are breathing might have a composition different from country air. But the movement of air, which is the wind and breezes, stirs up the atmosphere so that there is little difference in the percentages of oxygen and nitrogen in different samples. When you remember that a moderately stiff wind travels at say 25 miles an hour, it is not surprising that there are no marked differences in the air. It is found that when the air is quiet there may be slight differences in the composition of city air and country air. Accidental components may be present at times in rather startling amounts in city air on quiet days. For example, sulfur dioxide, SO_2 , and sulfur trioxide, SO_3 , are not detectable in country air, but in cities where coal is burned which has a rather high sulfur content, these two gases may be detected. The sulfur trioxide falls in rain as sulfuric acid and the sulfur dioxide as sulfurous acid. It is a common experience in crowded cities that many tender shrubs die from the effects of these sulfur compounds.

The oxygen cycle in nature is also responsible for the constancy of the composition of air. Although animals, man among them, use oxygen from the air and produce carbon dioxide, although furnaces and engines also decrease the oxygen and

increase the carbon dioxide in the air, the plants reverse this process. They use carbon dioxide and produce oxygen. These two components are maintained at a fairly constant level.

Composition of Dry Air

<i>Name</i>	<i>By Volume</i>	<i>By Weight</i>
Nitrogen	78.03%	75.88%
Oxygen	20.99	23.08
Argon	0.94	1.28
Carbon dioxide	0.03-0.04	0.045
Hydrogen	0.01	
Neon	0.0015	
Helium	0.0005	
Krypton	0.0001	
Xenon	0.00001	
Water	Varies greatly	

There is always more or less dust in the atmosphere. This dust is composed of tiny granules of soil, of small plant seeds and spores, of lint and fabrics, hairs and feathers. There are also a few bacteria in the air, although the number is quite small when compared with the number which will be present in a slow-moving stream of water.

The amount of moisture in the air varies with the temperature and the amount of evaporation which has occurred. If air is in contact with water for a sufficiently long period of time an equilibrium will be established between the liquid water and the gaseous molecules in the air. When this equilibrium is established, measurement of the amount of water in a given quantity of air shows that it has become constant. (The membership of molecules is changing, however. Some molecules are continually condensing on the liquid and some continually evaporating.) The air is *saturated* with water vapor. The quantity of water vapor which a given quantity of air will hold varies with the temperature. As the temperature increases, the capacity of the air for holding water vapor also increases. If air which is saturated with water vapor is cooled, water will precipitate either around dust particles as rain, fog, or mist, or on the sides of the container or buildings and clothing as a film of liquid.

The gaseous molecules of water in the air exert a pressure just as the gaseous molecules of any component of the air does. The

amount of water vapor which saturated air will hold at any temperature is usually expressed in terms of the pressure of the water vapor at that temperature. By the use of pressure units the volume of air need not be given, since the same pressure of water vapor will exist for any quantity of saturated air.

Humidity

The humidity is a measure of the amount of moisture in the air. It can be expressed quantitatively as the amount of water in a given quantity of air or by the pressure of the water in the air. This method gives the *absolute humidity*. *Absolute humidity is a measure of the quantity of moisture in the air.* In most weather reports the moisture is given in terms of the percentage of saturation. This is the *relative humidity*. If, for example, the relative humidity is 50 per cent and the temperature is 65° F. (18.3° C.), the vapor pressure will be 50 per cent of the vapor pressure of water in air which is saturated at 18.3° C. 15.5 mm. $\times 0.50 = 7.75$ mm. The atmosphere has a water vapor pressure of 7.75 millimeters.

The water vapor in the atmosphere cannot be seen since it is dispersed as molecules which are far too small for anyone ever to see. Steam is likewise invisible. It is only when droplets of water condense that they can be seen. The "steam" from the spout of a tea kettle is actually a cloud of droplets which has formed by the condensation of the steam and is not really steam at all. This cloud disappears rapidly because the tiny droplets evaporate into the air.

Human Comfort

Not only does human comfort depend on the temperature of the air in which man lives, but also on its composition. You have all had uncomfortable minutes in hot stuffy rooms. People have been actually ill and some have even died because of the composition of the air in which they were forced to remain.

Most of you may not know the story of the Black Hole of Calcutta, but you have all heard the term applied to small crowded rooms. On June 20, 1756, 146 English prisoners were placed in a small cell in Calcutta. The size of the room was 14 feet 10 inches by 18 feet. In June it is very hot in Calcutta and by morning 123 of the prisoners were dead.

What is it that makes one so uncomfortable in a small, crowded, poorly ventilated room? Various possible factors have been investigated. Most of you would immediately suspect that the amount of oxygen is the important factor. Everyone is using up oxygen, no matter how quietly he sits. But studies have shown that although the oxygen content of air falls in crowded rooms, discomfort occurs long before it is at dangerous levels. Man can exist at relatively low oxygen levels. When the oxygen falls to 17 per cent, a match will go out but a man will breathe fairly comfortably.

Is it the high carbon dioxide content which "poisons" men? Studies have shown that the carbon dioxide content of a crowded room may rise to 0.25 per cent. But subjects have breathed 2 per cent carbon dioxide for as long as 24 hours without any ill effects. It is not until the carbon dioxide content of air reaches approximately 4 per cent that evil effects develop.

You have all noticed the particularly offensive odor of a crowded, poorly ventilated room when you come into it. Some investigators have suspected that human beings may give off organic compounds in their breath and sweat which at high concentrations are toxic. This has also been tested with negative results.

In one experiment, subjects were confined in a small room and were provided with face masks through which they breathed pure air. Other subjects outside the room breathed air piped to their face masks from the room. The people who felt uncomfortable were those inside the room who were breathing pure air, while those outside breathing the "contaminated" air were comfortable. This experiment and others demonstrated that the discomfort in a poorly ventilated room comes from the high humidity. Our bodies give off moisture from the skin and lungs. Even when you are not sweating there is a large loss of moisture in expired air and some "insensible" perspiration from skin. When the air is still, you are soon enveloped in a sheath of air which is saturated with water. Evaporation of water is one of the means by which the body is cooled. When the room is hot to begin with, so that loss of heat by radiation and convection is poor, and when it is no longer possible to evaporate water at a rapid rate, loss of heat from the body falls to low levels. The temperature of the body begins to rise and discomfort, then illness, and finally death may result.

Comfort depends to as great an extent on the humidity of the air as on the temperature. Most people in the light winter clothing which Americans wear are as comfortable at 64° F. with a humidity of 55 per cent as they are at 70° F. with a humidity of 30 per cent. This represents a difficult problem in winter when the absolute humidity of the outside air is very low. If air is taken into the house and warmed, the relative humidity drops. If air has a relative humidity of 65 per cent at 35° F. (1.7° C.), it will have a vapor pressure of 6.1 millimeters. Suppose that this air is warmed to 70° F. without the addition of any water. At 70° F. (21.1° C.) the absolute humidity is 18.7 millimeters for saturated air.

$$\frac{6.1 \times 100}{18.7} = 32.6\% \text{ relative humidity}$$

You feel chilly when the humidity is low even though the temperature is rather high, because the rate of evaporation of water from your body is so fast that it has a distinctly cooling effect.

CHEMISTRY OF THE COMPOUNDS IN AIR

Nitrogen

Nitrogen is a colorless, odorless, tasteless gas at ordinary temperatures. When it is cooled and compressed, it is changed into a liquid. This liquid has a boiling point of -195.7°C. and a freezing point of -210.5°C.

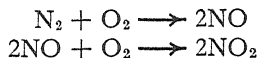
Chemically, pure nitrogen is very inert. The very fact that it occurs in such large quantities in the atmosphere shows that it is not reactive and does not combine with the compounds in the environment.

Nitrogen can be made to combine with hydrogen in the presence of a catalyst at moderately high temperatures and pressure.



This reaction is of great importance to the world, for by it inert atmospheric nitrogen is changed to a reactive compound, ammonia. Fertilizers and explosives are made from nitrogen "fixed" by this process.

Nitrogen combines with oxygen in the presence of a high-voltage discharge.



During thunderstorms, lightning causes this reaction to occur on a small scale. The nitrogen dioxide then reacts with water and falls to earth in the rain as nitric acid.



Needless to say, the quantity of NO_2 produced and the concentration of nitric acid in the rain is very low. The possibility of utilizing atmospheric nitrogen by this reaction is precluded in this country by the relatively high cost of electricity.

Nitrogen Cycle Some bacteria have the ability to utilize atmospheric nitrogen and to build it into useful compounds. Some bacteria produce nitrites and others form nitrates. Legumes are likely to have colonies of these organisms living on their roots in nodules. These bacteria are desirable because the nitrates and nitrites are used by plants. The growth of legumes enriches the soil by the addition of the nitrites or nitrates which have been formed by the bacteria on their roots.

Plants use the nitrites or nitrates produced in this way, or supplied by fertilizers, to form amino acids and then build protein. They can also use other nitrogen compounds such as

ammonia or ammonium salts. The source of these nitrogen compounds to plants is the decay of plants or animals after death and in manures, the excrement of animals.

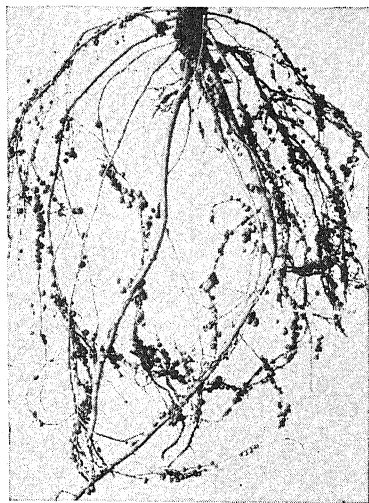
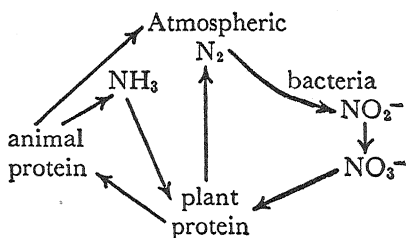


Fig. 21-2. Nodules of nitrogen-fixing bacteria on the roots of a soybean plant. (Bureau of Plant Industry, Soils, and Agricultural Engineering, U.S. Department of Agriculture.)

The nitrogen in plant protein which is not returned to the soil by decay of the plant may be used by an animal or by man as food. In the animal body the protein is digested and along with other compounds the amino acids which hold the protein nitrogen are absorbed. In the body of the animal, they may be built into his body protein or they may be used for energy and nitrogen compounds excreted in urine and feces.

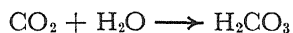
Some of the microorganisms which bring about the decay of dead plants and animals change nitrogen compounds into free nitrogen which escapes to the atmosphere. There are also soil organisms which change nitrogen compounds into free nitrogen so that it is no longer available to plants.

The nitrogen cycle maintains a kind of balance in nature and there is never an accumulation of one nitrogen compound or another or of free nitrogen. That the cycle does not maintain a perfect balance is shown by the tracts of worn-out land which occur even in our young country, the United States. Worn-out land is deficient in nitrogen as well as other compounds essential to good plant growth. Some plants take unusually large amounts of nitrogen compounds from the soil. When the plants are removed from the field, the nitrogen content of the soil gradually diminishes unless more is added by the farmer.



Carbon Dioxide

Carbon dioxide is a colorless, odorless gas at room temperature. It dissolves in an equal volume of water at 15°C . to produce a dilute solution of the weak acid, carbonic acid.



This solution has a faintly sour taste. Ordinary carbonated water or soda water effervesces with CO_2 , and most of you are familiar with its taste. When you smell carbon dioxide, you will

also notice this slightly sour taste at the back of your mouth as the gas dissolves in your saliva. You are familiar with the gas in all carbonated beverages and sodas and as the leavening agent in cakes, breads, and cookies.

Below 32° C., its critical temperature, the gas is changed into a colorless liquid when it is subjected to high pressures. This liquid carbon dioxide is marketed in cylinders. If the liquid is allowed to evaporate rapidly, so much heat is lost in the conversion of the liquid molecules to gas molecules that the temperature will fall below the freezing point and solid carbon dioxide snow is produced. You are undoubtedly familiar with solid carbon dioxide, known as "dry ice." It is commonly used in packing ice cream for home delivery and in refrigerating many other frozen products.

Carbon dioxide is not a poisonous gas, but if you were to breathe a mixture which was low in oxygen, you would suffocate. No animal can exist in an atmosphere of pure carbon dioxide because there is a deficiency of oxygen. In the laboratory there is no danger in preparing carbon dioxide and no precautions

need to be used to avoid breathing it. It is quite different in this property from the other oxide of carbon, carbon monoxide, which is very poisonous.

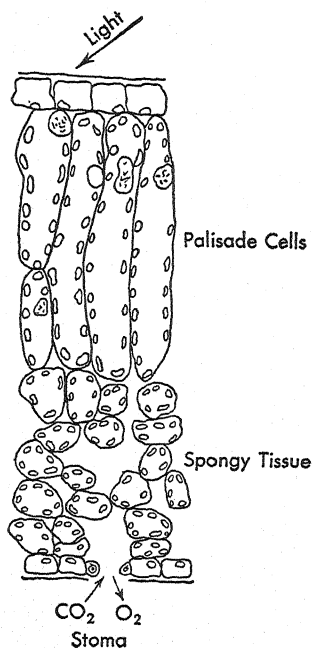
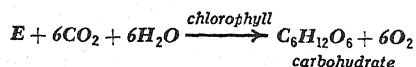


Fig. 21-3. Section of a leaf. The white bodies in the palisade cells and the spongy tissue are chloroplasts which contain chlorophyll. Carbon dioxide is extracted from the air and water from soil. When light falls on the leaf, the chlorophyll catalyzes the overall reaction:

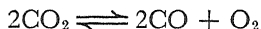


The oxygen is eliminated from the cells while the carbohydrate is stored.

Carbon dioxide, with a molecular weight of 44, is heavier than air. It tends to settle in low places, although it will diffuse through the atmosphere. When the flow of gas is continuous, layers rich in carbon dioxide will occur. This happens when carbon dioxide issues from fissures in the earth, in low places where air circulation is at a minimum.

Air contains a very small amount of carbon dioxide — just 0.035 volume per cent. But this volume of carbon dioxide is of great importance to plants. When sunlight falls on the green leaves of plants, they absorb carbon dioxide through the stoma of the leaves and, with water and the energy of the sun, they are able to build up complex molecules of carbohydrate.

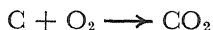
Carbon dioxide is a very stable molecule. If it is heated above 2000°C. , it will partially dissociate into carbon monoxide and oxygen:



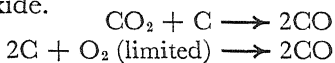
But at equilibrium, the amount of carbon monoxide is very small.

Preparation Carbon dioxide is readily prepared by a number of reactions.

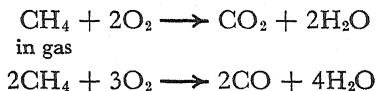
1. Carbon dioxide may be readily prepared by burning carbon in an excess of oxygen.



If there is not an excess of oxygen, the hot carbon may reduce the carbon dioxide to carbon monoxide or the union of carbon and oxygen may result in the formation of carbon monoxide instead of the dioxide.

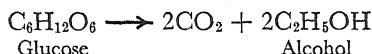


Many carbon compounds will also burn readily to produce carbon dioxide. Those in all petroleum products, in wood, paper, gas, and coal are compounds which are commonly burned. You are usually not concerned with the fact that carbon dioxide is the end product. But you are concerned with regulating the reaction so that there is enough oxygen in the mixture to carry the oxidation all the way to carbon dioxide and not stop at the poisonous carbon monoxide.

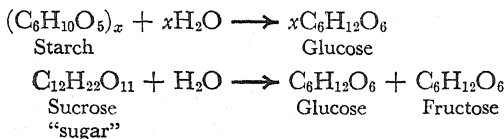


In a furnace or stove the amount of air admitted to the reaction through the drafts or the air vent must be sufficient to allow complete combustion to carbon dioxide. You have all read of tragedies which resulted from shutting down a fire too thoroughly. When this happens, carbon monoxide is produced and anyone in the vicinity is poisoned.

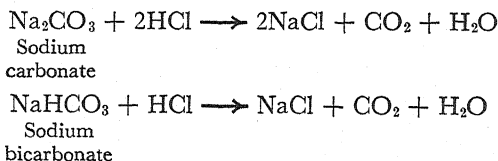
2. Fermentation. Carbon dioxide is one of the products of yeast fermentation of glucose. Alcohol, the other product of fermentation, is prepared in huge quantities for use as a starting material in organic syntheses, as a solvent, and in alcoholic beverages. Many large breweries and distilleries find it profitable to capture the carbon dioxide instead of allowing it to escape into the atmosphere. The fermentation process involves a series of reactions which are catalyzed by the enzymes produced by yeast cells. The overall reaction, the sum of the individual reactions, is:



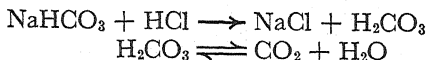
The glucose may be formed by the hydrolysis of starch in corn or potatoes, or by the hydrolysis of sucrose in molasses.



3. Carbonates and bicarbonates plus acid. Carbonates and bicarbonates will react with acids to produce a salt of the acid, carbon dioxide, and water:



It may be that the first product of the reaction is carbonic acid, H_2CO_3 , which then decomposes. Carbonic acid cannot exist in a concentrated solution, but decomposes to form carbon dioxide and water.

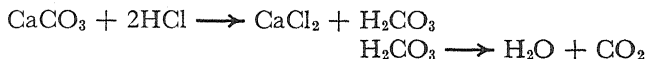


This reaction is of great importance in cooking. Baking soda is sodium bicarbonate, NaHCO_3 , and it is used in batters where there is some source of acid, such as sour milk or molasses. Baking soda is also one of the components of baking powders. They contain, along with the sodium bicarbonate, some acid salt or a salt which reacts with water to produce acid. When they are moistened, they begin to react, and carbon dioxide is produced. The bubbles of this gas leaven the batter and produce a porous structure which is easy to bite into.

Usually this method for the production of carbon dioxide on a small scale is used in laboratories. Calcium carbonate is frequently used as the carbonate since, in the form of limestone and marble chips, it is very cheap. The limestone and marble are not pure calcium carbonate, but the contaminants do not interfere with the production of carbon dioxide, and since it is a gas, it is readily separated from the reaction mixture.



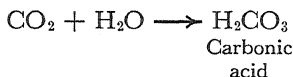
or



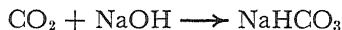
4. Decomposition of carbonates. Many carbonates, on heating, decompose to form an oxide and carbon dioxide. The calcium carbonate of limestone is very easily decomposed to produce quicklime, impure calcium oxide.



Reactions Carbon dioxide is an acid anhydride and reacts as they do — with water to form an acid or with bases to form salts.



Or with an excess of carbon dioxide:



Uses Carbon dioxide has many uses. Since it cannot burn, it is used in fire extinguishers. Some are simply cylinders of carbon dioxide gas or liquid carbon dioxide, which may be

released over a flame and which will smother it by cutting down the quantity of oxygen present. The more common fire extinguishers contain carbonates and a small vial of sulfuric acid. When the fire extinguisher is turned upside down, the sulfuric

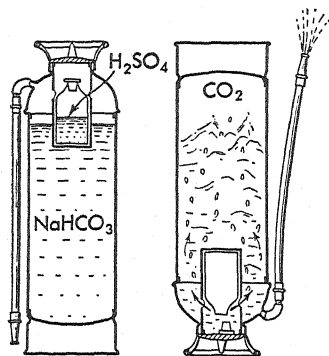


Fig. 21-4. Fire extinguisher. When the extinguisher is turned upside down, H_2SO_4 is released which reacts with NaHCO_3 to form CO_2 . The CO_2 forces the mixture out of the hose. The solution saturated with CO_2 extinguishes the fire because both water and CO_2 exclude oxygen of the air.

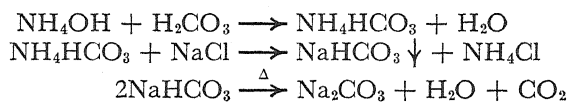
acid comes in contact with the carbonate and a large volume of carbon dioxide is released. The extinguisher is easily recharged by washing out the cylinder, adding sodium carbonate and filling the vial with sulfuric acid again. Some carbon dioxide fire extinguishers contain a colloidal agent as well as the carbonate and acid. When the carbon dioxide is produced, a foam is formed and instead of a gas blanket, a carbon dioxide foam flows out of the nozzle and over the fire. The foam holds the carbon dioxide close to the burning material and is very efficient in quickly smothering the fire.

Large quantities of carbon dioxide are used in the soft drink industry. A soft drink is a sugar solution, often with some organic acid such as citric acid, and with flavoring and color added. The solution is "carbonated" by adding carbon dioxide under pressure.

You are familiar with the use of "dry ice," or solid carbon dioxide. It is used extensively for packing ice cream for home delivery. The "dry ice" sublimates at -79°C ., and the ice cream mixtures, which have melting points below zero, are kept well frozen as long as some carbon dioxide remains. Indeed, the ice cream is kept completely solid. Most of you have had the frustrating experience of trying to cut ice cream immediately after removing it from "dry ice." "Dry ice" is also used as a refriger-

ant when temperatures below zero are needed and when the weight of water, the bother of melting ice, or the presence of moisture must be avoided.

In 1948, carbon dioxide was used in the production of 4,575,452 short tons of sodium carbonate by the Solvay process. You may be astonished at such a large consumption and may immediately wonder at the quantity of "soda," sodium carbonate, which is produced. This compound is used in great amounts in many industries. A few are those producing glass, soap, paper, leather, dyeing, oil refining, and water softening. The Solvay process is a very economical one in which ammonium hydroxide reacts with carbonic acid to form ammonium bicarbonate. This, in turn, reacts with sodium chloride to form sodium bicarbonate which is fairly insoluble in the salt solution. The sodium bicarbonate is removed and on heating is converted to sodium carbonate. The Solvay process is:



The process is carefully worked out to utilize all the byproducts of the reaction.

The Rare Gases

The rare gases are the elements present in the atmosphere in very small quantities. They are all members of the family of inert gases, family O, and include helium, neon, argon, krypton, and xenon. Radon is also a member of the family, but it is not ordinarily detectable in the atmosphere. It is the radioactive member of the family.

Helium was discovered on the sun during the solar eclipse of 1868 by Lockyer and Janssen. Does this surprise you? Helium is a component of the atmosphere, yet it was first discovered on the sun, millions of miles away. It all happened through the use of the spectroscope. A very hot gas gives off light of definite wavelengths which are characteristic of the elements present. For example, sodium gives off a yellow light and any compound of sodium which is heated hot enough will give off this yellow light. A spectroscope separates the wavelengths of light and

makes it possible to identify the elements present in a hot gas. When Lockyer and Janssen examined pictures of the sun's

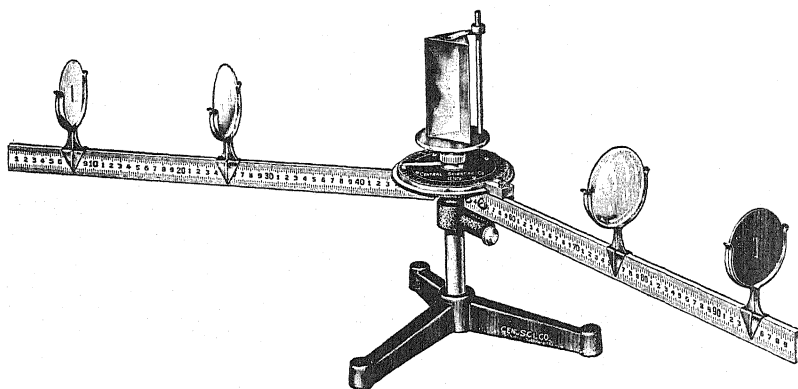


Fig. 21-5. Spectrometer. The substance to be analyzed is heated and the light emitted from the material is viewed through the slit. The refracting prism separates the various wavelengths of light. The emission spectrum is characteristic of the element. (Courtesy of Central Scientific Company.)

corona, they found lines of an element which was unknown to them.

Rare Gases

<i>Gas</i>	<i>Parts per million in dry air</i>
Helium	3
Neon	12
Argon	9400
Krypton	0.5
Xenon	0.06

They did not have any idea what its properties were, but they did know that this element occurred in the extremely hot atmosphere of the sun, and they therefore named it helium. It was discovered in the earth's atmosphere when Ramsey and Raleigh fractionated the small residue of rare gases which were left after the removal of oxygen, nitrogen, carbon dioxide, and water from air.

Helium also occurs in some rocks and some natural gases. You will remember that this element is given off by radioactive elements as an alpha particle. Undoubtedly the source of the

helium in the earth is the radioactive disintegration which has been occurring for centuries. The helium in natural gases is removed by fractionation. It has the very low boiling point of -272°C .

Helium is used in lighter-than-air craft since it has great buoyancy and yet will not burn. The buoyancy of a gas depends on its density compared to air. Helium has a density of 4 grams per 22.4 liters at standard conditions, while hydrogen is 2 grams per 22.4 liters, and air is 29.06 grams per 22.4 liters. Hydrogen is more buoyant than helium, but it explodes readily in air and is, therefore, much less desirable than helium.

Helium is also used in an oxygen-helium mixture in place of air for deep-water workers. When a man works at a depth of, say, 25 feet of water, he is subjected to the pressure of the air plus the pressure of the water above him. The gases which he breathes into his lungs dissolve in his blood to a greater extent than they do at normal pressures. When the worker is raised to the surface of the water, the pressure on him is decreased and the solubility of gases in his blood also decreases. Oxygen is used by his tissues and does not present a problem, but nitrogen escapes from the blood stream in tiny bubbles. When a bubble is released in a muscle, it causes severe pain. Bubbles released in some parts of the worker's body may even endanger his life. This is called "bends." Helium is much less soluble than nitrogen and, therefore, when a worker who has breathed helium and oxygen is raised to the surface, the size of the bubbles released is much smaller.

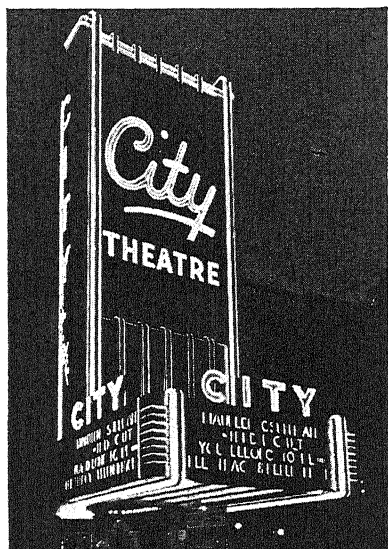


Fig. 21-6. Neon lights are now characteristic of our cities. (Courtesy of the Linde Air Products Company.)

The other rare gases were discovered when Raleigh and Ramsey fractionated the residue from air after they had removed the known elements and compounds, oxygen and nitrogen and carbon dioxide and water.

Neon is widely used in signs. When a small amount of neon is introduced into an evacuated tube and an electric current is passed through, the neon glows with a very bright red color. You are all familiar with it. The color may be varied by introducing other gases, which will also glow with their characteristic color, or by coloring the glass.

Argon is used to fill electric light bulbs in order that the filament will not react, crumble, and break when it is heated to a glow.

NEW TERMS

Atmosphere, absolute humidity, relative humidity, nitrogen cycle.

QUESTIONS

1. How can we show that the atmosphere is a mixture and not a compound?
2. What is the composition of the atmosphere? What is the function of each one of the components?
3. Why does the amount of carbon dioxide and of oxygen remain relatively constant in the atmosphere?
4. How does the composition of the atmosphere at sea level compare with that on the top of a high mountain?
5. What change in the composition of the air accounts for the stuffy feeling of a hot, closed room with a number of people in it?
6. Why is the air of most of our homes very dry (low humidity) in winter? What effect does this have on our comfort?
7. Describe the nitrogen cycle in nature. Why are some soils more fertile than others?
8. Give two methods for the preparation of carbon dioxide.
9. Give the equation for the reaction of carbon dioxide and a hydroxide.
10. Give some of the uses of carbon dioxide.
11. What is "dry ice"? How is it used?
12. What are the rare gases? Why are they given this name? Give the uses for the rare gases. Do they form compounds? How does the Atomic Theory account for this?

ORGANIC CHEMISTRY

Compounds and Reactions

Organic chemistry is the study of the properties and chemical reactions of compounds containing carbon. The study of all other compounds is called inorganic chemistry. There are three important reasons why the compounds of one element are separated and studied as a distinct branch of chemistry:

1. The reactions of organic compounds are distinctly different from the reactions of the compounds of other elements. For one thing, many of the reactions are slow equilibrium reactions. Instead of the split-second speed of an inorganic reaction such as that of sodium chloride and silver nitrate, many organic reactions require hours or even days to produce an appreciable amount of produce.

Inorganic: $\text{NaCl} + \text{AgNO}_3 \longrightarrow \text{AgCl} + \text{NaNO}_3$ very rapid

Organic: Acetic acid + Methyl alcohol \longrightarrow

Methyl acetate + H_2O slow

Many inorganic reactions will go practically to completion while many organic reactions form equilibriums in which some of the reactants are always present.

2. The compounds of carbon are generally more complex than inorganic compounds. For example, there is only one compound composed of hydrogen and chlorine, i.e., HCl , while there are two composed of hydrogen and oxygen, i.e., H_2O and H_2O_2 . But there are hundreds of compounds composed of carbon and hydrogen. This great number of compounds results from the ability of carbon atoms to link one to the other in compounds. Few elements have this property, and none has it to the extent shown by carbon.

3. The total number of compounds of carbon is much larger than the total number of compounds of all other elements. It has been estimated that there are perhaps 300,000 organic

compounds while there are approximately 50,000 inorganic compounds.

History

During the eighteenth century men working in laboratories began to isolate compounds from all sorts of material in their environment. In general, the compounds were classified according to their source. Thus compounds isolated from cells, which make up the animal or vegetable kingdom, were called "organic compounds" while those isolated from inanimate material were classified as "inorganic." Of course, such a classification became impractical when knowledge grew, because many compounds occur both in animate and in inanimate objects. Salt, NaCl, was found, for example, in sea water (therefore inorganic) as well as in blood (therefore organic). This method of classification was abandoned, but the terms were retained. Now "organic compound" means a compound of carbon and whether or not it has been isolated from a cell is not considered.

In the early days, organic compounds were considered unique. The awe which everyone feels for the process of life caused early investigators to expect that compounds isolated from living material were different in kind from other compounds. It was believed that organic compounds could not be synthesized unless a "vital force" was present. It was not known what made up "vital force," but it was believed that this was a mystic property of living cells.

In 1828 Wöhler, a German chemist, accidentally synthesized the white crystalline compound, urea, NH_2CONH_2 , found in urine. He recognized the significance of this chance reaction: he had synthesized an organic compound without the presence of a living cell. For twenty years an argument raged between those who believed in the need of "vital force" for the synthesis of organic compounds and those who did not. Finally by 1850, so many organic compounds had been synthesized in the laboratory that the "vital force" theory was dead.

Properties of Organic Compounds

1. Elements. Organic compounds always contain carbon, usually contain hydrogen, and frequently contain oxygen.

Other elements which are present in a moderate number of compounds are nitrogen, sulfur, phosphorus, and the halogens.

2. Combustibility. Most organic compounds are combustible. If an aspirin tablet or some sugar is heated, it will char and burn. Inorganic compounds do not commonly have this property. This is, then, a simple way for differentiating most organic compounds from inorganic compounds.

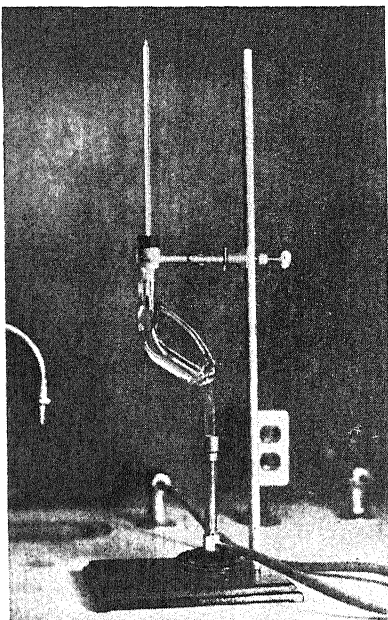
3. Molecular weights. Some organic compounds have enormous molecular weights, running into the millions. No inorganic compounds have even moderately high molecular weights.

4. Melting and boiling points. In general the melting and boiling points of many organic compounds are low. You are familiar with the fact that you can readily melt sugar in a frying pan on a cook stove while you cannot melt salt at the temperature obtainable here.

5. Solubility. Many organic compounds show low solubility in water, but are soluble in organic liquids such as benzene, ethyl alcohol, and acetone.

6. Ionization. Ionization is commonly completely lacking in organic compounds. In other words, the bonds between the atoms which make

Fig. 22-1. Determining the melting point of an organic compound. Most organic compounds have relatively low melting points which are characteristic of them. This apparatus is well suited to determining the melting point. It is filled with oil or sulfuric acid and the temperature is raised slowly and uniformly by heating the tube at the low point. The peculiar shape of the tube creates heat currents through the liquid which stirs it. The solid is in a capillary tube attached to the thermometer.

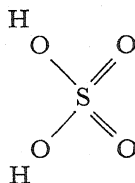


up organic compounds are covalent. When ionization does occur in an organic compound, it is usually very weak.

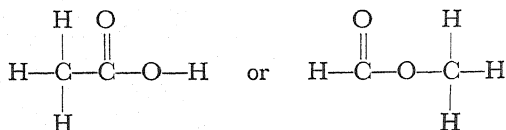
7. Isomerism. Isomerism is the occurrence of two or more compounds with the same molecular formula but different structural formulas. This is a very common phenomenon in organic chemistry. Thus:

<i>Molecular Formula</i>	<i>Number of Compounds</i>
H_2SO_4	1
$\text{C}_2\text{H}_4\text{O}_2$	4
$\text{C}_8\text{H}_{12}\text{O}_4$	105

The molecular formula H_2SO_4 stands for just one structure



and when " H_2SO_4 " is written, it always refers to this structure. But $\text{C}_2\text{H}_4\text{O}_2$ stands for



The lines between the atoms represent valence bonds. These are *structural* formulas and are commonly used in organic chemistry.

Scope

Most of you are familiar with the scope of organic chemistry and are aware that it has profound effect on your lives. Many of the materials of your environment are composed of mixtures of organic compounds and a few are simple compounds. Thus the food you eat is a complex mixture of organic compounds, water, and inorganic salts. The molecules which make up the fabric of your clothing, whether cotton, rayon, silk, wool, or linen,

are organic compounds. The dyes which color them are organic. Wood, rubber, coal, and petroleum are all organic mixtures. Your bodies are composed of both organic and inorganic molecules. The drugs you use when you are ill are mostly organic compounds. So in all phases of daily life organic compounds are constantly being used.

Source

A great many of the organic compounds which you use are produced in nature through the chemical processes of cells. Others are synthesized in the laboratory, but the starting materials are usually themselves organic compounds which have been produced by cells. It is far cheaper and certainly more convenient to allow plant cells to use simple substances such as carbon dioxide, water, and ammonia and build them up into organic compounds. Coal and petroleum, which are the chief sources of compounds for synthetic organic chemistry, are the products of plants which lived centuries ago. In nature there are in readily obtainable state the following:

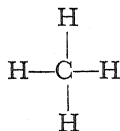
1. Petroleum and coal (chief source)
2. Fibers — wood, wool, cotton, etc.
3. Seed oils — cotton, corn, tung, soy bean, etc.
4. Other oils — whale, bone, etc.
5. Alkaloids — quinine, strychnine, etc.
6. Starches, sugars, etc.

Structure

Empirical Formula You will remember that the empirical formula of a compound gives the elements and their *relative* number in one molecule while the molecular formula gives the elements and the actual number of atoms in the compound. The empirical formula may be calculated from the data obtained by analyzing the compound quantitatively for each element. If the molecular weight is also known the molecular formula may be calculated (see section on calculation of formula, Chapter 2).

Carbon has a valence of four. Since this is a covalence, it means that each carbon atom shares the four electrons in its outer orbit with other elements and in its turn it shares four

electrons from other elements. (See section on valence, Chapter 8.) Thus in methane, CH_4 , the structural formula is:



and by that it is meant that the carbon is sharing one of its valence electrons with each of the hydrogens and that each hydrogen is sharing its electrons with the carbon



The bonds between these elements are all covalent bonds. If the electrons in the outermost orbit of each atom are shown, the diagram is:

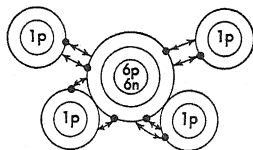
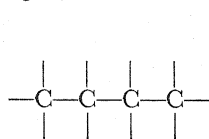
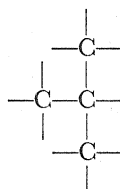


Fig. 22-2. Methane, CH_4 .

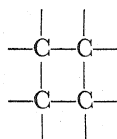
Some compounds contain a chain of carbon atoms and each carbon atom shares electrons with a neighboring carbon and thereby holds the molecule together. Some of these chains are straight, some are branched and some are closed rings.



Straight chain



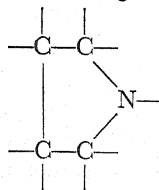
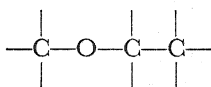
Branched chain



Closed chain

(The other elements in the compounds are omitted since they will vary from one compound to another.)

Some organic compounds exist in which other elements make part of the chain or ring. For example sulfur, nitrogen, or oxygen may be included as in the chain and ring below:



The valence of oxygen is two, nitrogen three, and sulfur two, occasionally four or six, and these are covalences.

The structural formulas will be written in two dimensions on the plane of the sheet of paper. Actually, of course, molecules are three-dimensional objects, and if their true structure were to be shown it would be necessary through projection drawings to indicate three dimensions. This is not very convenient in a text-book or notebook. The three-dimensional figure will, then, be projected into two dimensions. When the carbon with its

valence bonds is written $\begin{array}{c} | \\ -\text{C}- \\ | \end{array}$, a flat two-dimensional figure

results. As it exists in space it is more like a tetrahedron with the carbon at the center, the valence forces radiating out equally in three-dimensional space, and the elements to which it is joined the points of the tetrahedron:

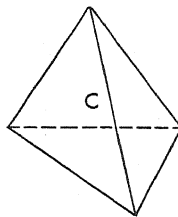


Fig. 22-3. Tetrahedron.

A so-called straight chain of carbon atoms is only straight when it is written on a flat surface. In reality the chain is crooked.

Thus a chain

of three carbons, $\begin{array}{c} | & | & | \\ -\text{C} & -\text{C} & -\text{C}- \\ | & | & | \end{array}$, would be:

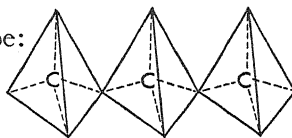


Fig. 22-4. A carbon chain.

If one were to try to draw the three-dimensional relationships of the atoms in a fairly complicated molecule, it would be very difficult to follow. Therefore, structural or graphic formulas will be used, which are two-dimensional and which emphasize the connections of one atom with another, but not their actual space relationships to one another.

THE HYDROCARBONS

Hydrocarbons are organic compounds composed of the two elements, hydrogen and carbon. Since they contain only these

two elements, they are relatively simple compounds. They will be the starting point and then more complex ones will follow.

In this way, by starting with simple compounds and advancing to more difficult ones, you will find that organic chemistry is well organized and easy to grasp. You must, however, understand each step that is taken, and you must memorize some organic names and structures. If you do the first steps thoroughly, you will find that the rest is easy. Be systematic. Study each part thoroughly before you proceed to the next.

There are many groups of hydrocarbons. The most important are the aliphatic and aromatic hydrocarbons. The aliphatic hydrocarbons are chain compounds, either straight chain or branched. The aromatic hydrocarbons contain rings of carbon atoms. The name "aliphatic" comes from the fact that fats produce straight-chain acids on hydrolysis. The name "aromatic" is derived from the fact that many ring compounds have pleasant, aromatic odors.

The group of aliphatic hydrocarbons is composed of a number of series of compounds closely related to one another. Each series is called a homologous series. *A homologous series is a group of organic compounds containing the same general formula and possessing similar physical and chemical properties.* It is possible to study one or two members of a homologous series, and, by this study, have a fairly good idea of the chemical and physical properties of all the other members of the series. This means that even though there are over 300,000 organic compounds, it is possible to obtain a working knowledge of a large number by studying the reactions of a rather small number. The physical properties of members of a homologous series, homologs, show gradual change as the molecular weight increases. The homologs with high molecular weight will be solids, while those with lower molecular weights will be liquids or even gases.

The *general formula* shows the elements in the homologs and the ratio of their number. C_nH_{2n+2} is, for example, the general formula for the members of the paraffin series. It means that the number of hydrogen atoms in any one compound is equal to twice the number of carbon atoms plus two. Thus a homolog with two carbon atoms will have six hydrogen atoms ($2 \times 2 + 2 = 6$); one with ten carbon atoms will have 22

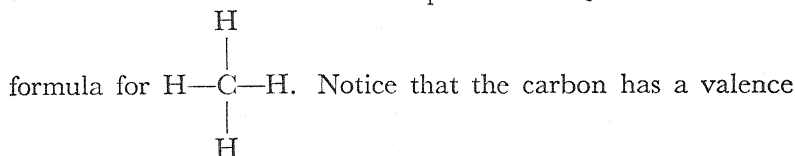
hydrogen atoms; and one with 15 carbon atoms will have 32 hydrogen atoms.

The Paraffins or Alkanes

The paraffins are a homologous series of aliphatic hydrocarbons which will be studied first. They will serve to teach you the basic nomenclature of organic chemistry and to illustrate the relationships between homologs. The paraffins are given this name because they are quite unreactive. The name comes from the Latin words *parum affinis*, which means literally "little akin." The general formula of the paraffins is C_nH_{2n+2} and the low molecular weight members of the series have molecular formulas of the following:

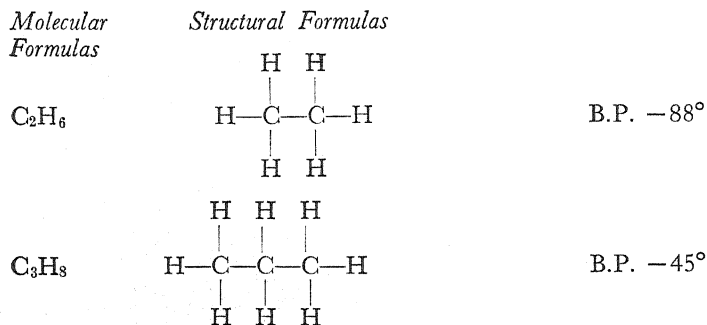


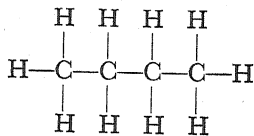
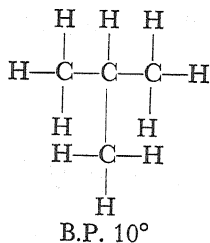
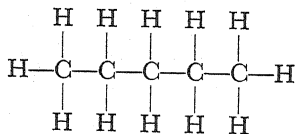
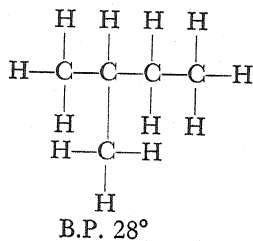
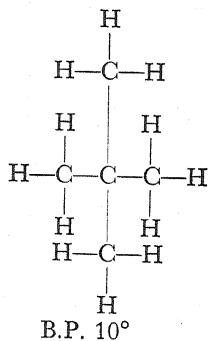
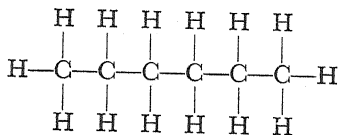
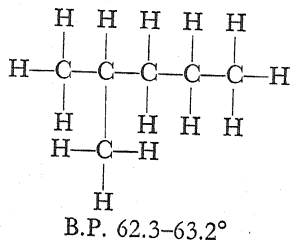
Isomerism occurs in these compounds, so that the molecular formula may give the composition of more than one compound. It is the structural formula which is significant and which shows the difference between similar compounds. CH_4 is the molecular

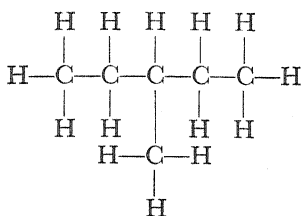


of four and the hydrogens each have a valence of one. These are covalences. There is a sharing of two electrons between each hydrogen and the carbon.

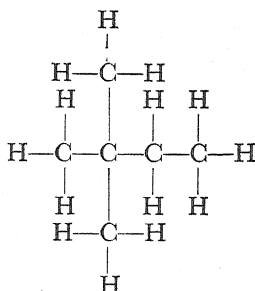
The structures of the other homologs are:



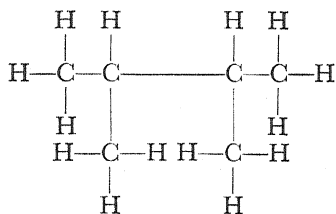
C_4H_{10} B.P. 0.6° B.P. 10° C_5H_{12} B.P. 36° B.P. 28° B.P. 10° C_6H_{14} B.P. 69° B.P. $62.3-63.2^{\circ}$



B.P. 63.2°



B.P. 49-50°



B.P. 58°

There are several systems of naming these compounds, but the simplest is the Geneva or International Union of Chemistry (I.U.C.) name. In 1892 a group of chemists from many countries met in Geneva, Switzerland, to try to systematize the nomenclature of organic compounds. They hoped to devise a system whereby the name of a compound would be the same all over the world.

For some compounds the old-fashioned names are still used, particularly in nutrition, medicine, and biochemistry. Organic chemists more and more use the easily learned and easily understood Geneva or I.U.C. names.

The rules for naming members of the paraffin series are as follows:

1. The root of the name comes from the longest carbon chain.

meth- = one carbon
 eth- = two carbons
 prop- = three "
 but- = four "
 pent- = five "

hex- = six carbons
 hept- = seven "
 oct- = eight "
 non- = nine "
 dec- = ten "

Notice that the roots for the number of carbons above four are the Greek or Latin roots which you already know in words like pentagon and octave. Above ten use the Latin roots.

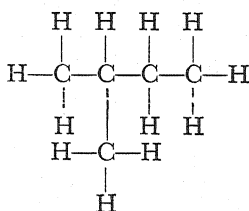
2. Use the ending “-ane” to indicate that the compound is a paraffin or a paraffin derivative.

3. Parts of molecule not already named are named as radicals:

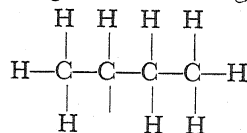
H HC—	methyl	Cl—	chloro or chlor
H HH HCC—	ethyl	Br—	bromo or brom
HH HCC—		I—	iodo
HHH HCCC—	propyl	—OH	hydroxy
HHH			

These use the same roots as indicated in rule 1.

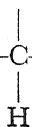
4. Number the carbon chain either from left to right or from right to left, but use only one system at a time. Indicate the position of the radical by preceding the radical name by the number of the carbon to which it is attached, as “2-methyl.” Use only one number system, but use the one which gives the smallest numbers in the name. Example:



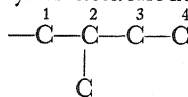
The longest chain has four carbons, which gives the root “but-.” Since the compound is a paraffin, C_5H_{12} , it is given the ending “-ane.” Butane names this part



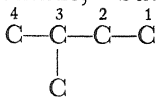
but does not name $\text{H}-\text{C}-\text{H}$. This is the methyl radical, and



it is necessary to show to which carbon the methyl is attached. If the chain is numbered from left to right

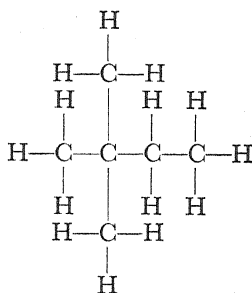


the name is "2-methyl butane," but if the chain is numbered from right to left,

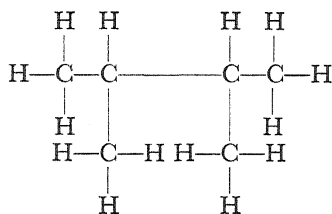


it is "3-methyl butane."

The first name is correct since it uses the smaller number.



This is 2-2-dimethyl butane. The "di-" shows that there are two methyl groups, and the numbers "2-2-" indicate that both methyl groups are attached to the 2 carbon.



This is 2-3-dimethyl butane.

The Geneva or I.U.C. names for the compounds listed previously are:

- C_2H_6 ethane
- C_3H_8 propane
- C_4H_{10} butane and methyl-propane (or 2-methyl propane)
- C_5H_{12} pentane, 2-methyl butane, and 2-2-dimethyl propane
- C_6H_{14} hexane, 2-methyl pentane, 3-methyl pentane, 2-2-dimethyl butane, 2-3-dimethyl butane

These same rules apply, with slight modifications, to all organic compounds. If you master these, you will be able to understand the names of organic compounds, and what is perhaps more important, you will gain an ability to mentally dissect the structure of an organic compound and quickly grasp the relations of one atom to another. Since they are simple compounds, it is easiest to introduce you to organic chemistry and some of its rules through these compounds.

Occurrence The most important source of these hydrocarbons is in petroleum or the natural gas associated with it. Petroleum is a complex mixture of organic compounds. All petroleum has members of the paraffin hydrocarbons, but they also contain olefin hydrocarbons (see below), hydrocarbons with ring structures and small amounts of compounds which contain oxygen, nitrogen, or sulfur, as well as carbon and hydrogen. Petroleum from different parts of the country differs in the relative amounts of these compounds. Some petroleum has rather large amounts of the ring compounds, while other petroleum has very small amounts.

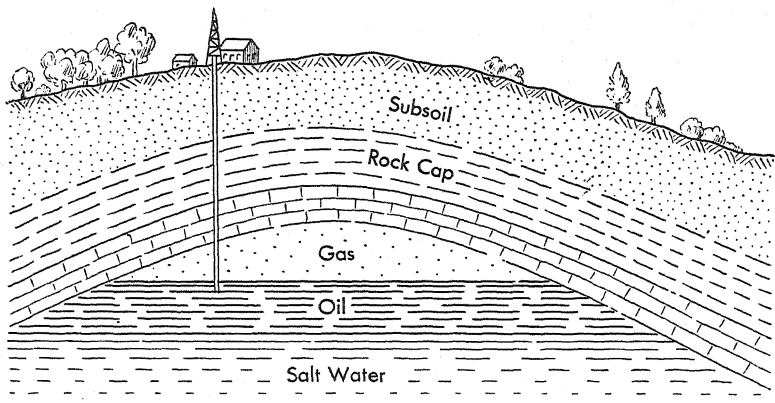


Fig. 22-5. Occurrence of crude oil. Often the oil is trapped below layers of earth. It often floats on salt water and is covered by an atmosphere of the more volatile hydrocarbons, the "natural gas."

The natural gas, which usually caps the pools of oil in the earth, is made up of the more volatile members of the hydrocarbons — those which exist as gases at ordinary temperatures and those which have rather low boiling points and a consider-

able vapor pressure at these temperatures. Methane is the most common compound in natural gas, but there is also ethane, and butane, with small amounts of other paraffin hydrocarbons up through the octanes.

SOURCES OF ALIPHATIC CHEMICALS

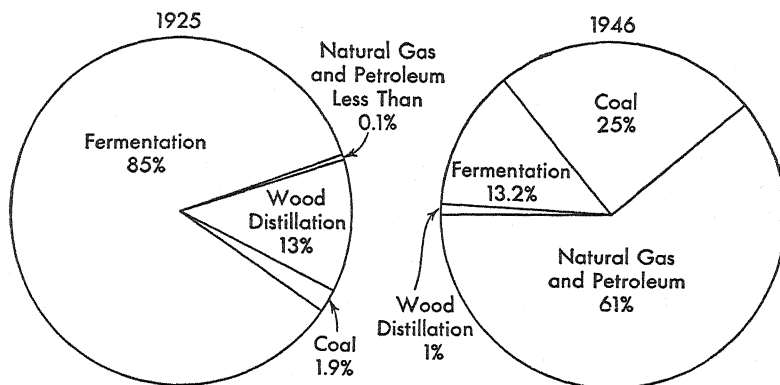


Fig. 22-6. Courtesy of Union Carbide and Carbon Corporation.

Methane is formed during the decay of plant or animal tissue. The gas which bubbles out of marshes has a high percentage of methane in it. Methane was discovered long ago and given the name of "marsh gas." For centuries, people have been superstitiously afraid of marshes where "ghosts" wandered at night. The "ghosts" have frequently been methane fires burning with a small flickering light. But methane is given off from most decaying tissue. The noxious odor of putrefaction is caused by a mixture of gases, one of which is methane.

On distillation of petroleum, some fractionation of the mixture is achieved. Crude oil is distilled from huge continuous stills and the components separated according to their boiling points. The low boiling components are the low molecular weight members of the paraffin and olefin hydrocarbons. Compounds with higher molecular weights have higher boiling points, until finally at the other end of the scale, there are compounds which will not boil without decomposing. These have high molecular weights. The petroleum is not fractionated into pure compounds, but into mixtures of compounds with similar boiling points. The exact boiling point range of the fractions differs from one refining company to another and varies with

the source of the crude oil. Usually the first fraction contains those compounds which boil below 70° C. and is called "petroleum ether" or "ligroin." The next fraction, up to about 200° C. is the "gasoline" fraction. Then comes "kerosene," then fuel oils and lubricating oils. Paraffin is left in the still from some oils, asphalts from others. Greases are the mixture of paraffins left in the pot with small amounts of liquid hydrocarbons. The paraffin which is used on jellies and which coats "waxed" paper is a purified mixture of these hydrocarbons. "Mineral oil" is a highly purified, high-boiling fraction of petroleum.

Some Commercial Products from Petroleum *

<i>Commercial Name</i>	<i>Approximate Composition</i>	<i>Boiling-Point Range</i>	<i>Uses</i>
Petroleum ether	C ₄ to C ₇	35°–80°	Solvent (laboratory)
Gasoline	C ₄ to C ₁₃	40°–225°	Motor fuel
Naphthas (many grades differing in volatility)	C ₄ to C ₁₃	40°–225°	Solvents — for paints, varnishes, rubber, extraction of fats
Kerosene	C ₁₀ to C ₁₆	175°–300°	Lighting, fuel
Lubricating oils (many grades differing in viscosity)	C ₂₀ up	350° up	Lubrication
Paraffin (several grades differing in M.P.)	C ₂₃ to C ₂₉	50°–60° M.P.	Candles, waterproofing, as waxed paper, etc.
Asphalts		Viscous liquids to 150° M.P.	Paving, roofing, fuel
Coke			Fuel

* Hopkins and Bailar: *Essentials of General Chemistry*, copyright 1946 by D. C. Heath and Co. and used with their permission.

Many of the fractions from petroleum are carefully refined or purified before they are sold. Most gasoline direct from the stills contains compounds which may produce gums on combustion, or compounds with objectionable odors, or substances which cause excessive knocking. These are carefully removed before the gasoline is ready for market.

Octane Numbers In a high-compression gasoline engine, such as those in present-day automobiles, the efficiency depends for one thing on the ability of the gasoline to burn without excessive knocking. When the gasoline burns in the cylinder, it pro-

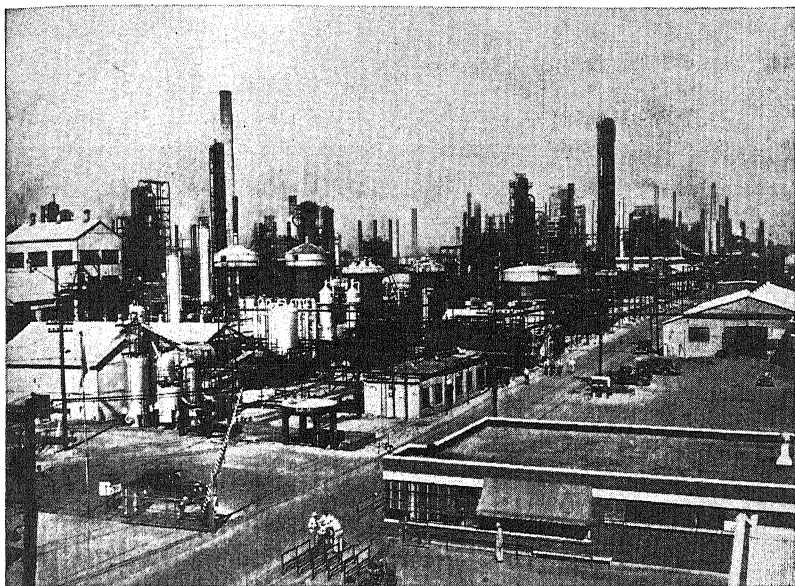
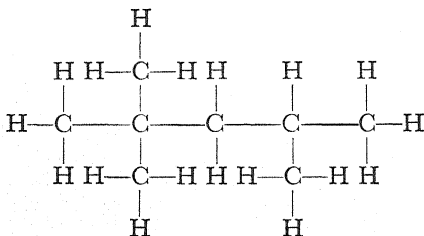
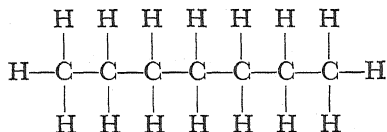


Fig. 22-7. Oil Refinery. This mass of pipes, smoke stacks, still heads, and tanks includes equipment for the distillation of petroleum to produce gasoline, kerosene, fuel oil, lubricants and a great number of other products. Thermal cracking units are also included. (Courtesy of Shell Oil Company.)

duces a large amount of hot gas which pushes the piston out of the cylinder in a power stroke. In a smooth running engine, first one piston and then another are pushed out smoothly to propel the automobile. If "knocking" occurs during the burning of the gasoline in the cylinder, the piston will be pushed out in jerks. It was necessary in the development of the high-compression gasoline engine to have some means of measuring the performance of a gasoline. The *octane number* does this. At the time it was developed, the octane, 2-2-4 trimethyl pentane



gave the best performance, while heptane



gave the poorest, or the most knocking. A scale was devised in which the octane was numbered 100 and the heptane 0. A gasoline which performs as well as a mixture of 20% octane and 80% heptane has an *octane number* of 20. Aviation gasoline is now made with an octane number of 120. In other words, it has a performance better than pure 2-2-4 trimethyl pentane. (The scale is extended and carefully calibrated. Explanation of it is beyond the scope of this book.) In 1922 it was discovered that the addition of small amounts of lead tetra ethyl to gasolines diminished their tendency to knock, or improved their octane number. "Regular" gasoline, as well as "ethyl" gasoline, now has this compound added. "Ethyl" gasoline has a higher octane number than "regular," but this will vary. During World War II, the octane number of all gasolines was decreased, in line with the need for high octane gasoline for aircraft. One gasoline company recently marked their pumps with the octane number. "Regular" gasoline was marked, "Not below 72 octane number," while "Ethyl" was marked, "Not below 79 octane number."

Olefins or Alkenes

The olefins are a homologous series of hydrocarbons with the general formula, C_nH_{2n} . They are important to study because they contain a linkage which occurs in many other compounds, an *unsaturation*. An unsaturation is a bond in which four electrons are shared between two carbons. Example: $\text{x}\ddot{\text{C}}\text{:}\ddot{\text{C}}\text{x}$ The electrons represented as *x* are those which the carbons share with some other element. In the paraffin series, you will remember, each carbon shares a pair of electrons with the carbons or hydrogens to which it is linked. (Look back at the formula for methane, CH_4 , on p. 336.) This pair of electrons is the *chemical bond*. Since, in the example of the olefin given above, the carbons

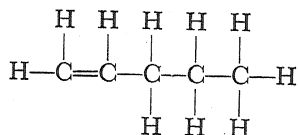
are sharing *four* electrons, there are two chemical bonds, or a *double bond*. A double bond is the sharing of four electrons by two elements. These bonds are indicated with the lines used in

other formulas $\begin{array}{c} | & | \\ -C & =C- \end{array}$. All members of the olefin series have one double bond.

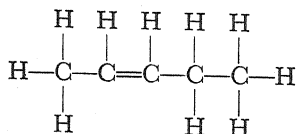
The low molecular weight members of this series have the following molecular and structural formulas. Their names are also given and are explained below.

Olefins C_nH_{2n}

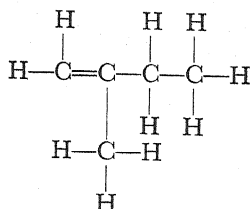
		<i>I.U.C. Name</i>	<i>Common Name</i>
CH_2	No compound known		
C_2H_4	$\begin{array}{c} H & H \\ & \\ H-C & =C-H \end{array}$	Ethene	Ethylene
C_3H_6	$\begin{array}{c} H & H & H \\ & & \\ H-C & -C=C-H \\ \\ H \end{array}$	Propene	Propylene
C_4H_8	$\begin{array}{c} H & H & H & H \\ & & & \\ H-C & =C-C-C-H \\ & & & \\ & & H & H \end{array}$	Butene-1	Butylenes
	$\begin{array}{c} H & H & H & H \\ & & & \\ H-C & -C=C-C-H \\ & & & \\ H & & & H \end{array}$	Butene-2	
	$\begin{array}{c} H & & H \\ & & \\ H-C & -C=C-H \\ & \\ H-C-H \\ \\ H \end{array}$	Methyl propene	

C_5H_{10} 

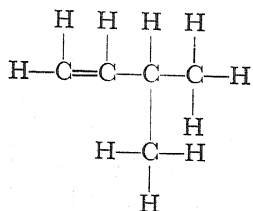
Pentene-1



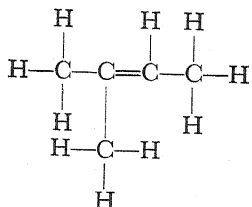
Pentene-2



2-Methyl butene-1



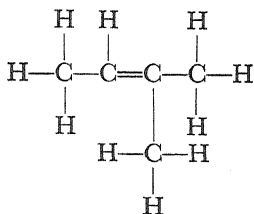
3-Methyl butene-1



2-Methyl butene-2

Amylenes

Look at these formulas carefully. They represent all the isomers for each molecular formula. All these compounds, except CH_2 , are known. Any other formulas which you might write which have the same molecular formula are one of these structural formulas turned around. For example,



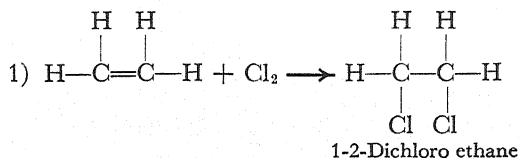
is 2-methyl butene-2 and is the same as the last formula rotated halfway round.

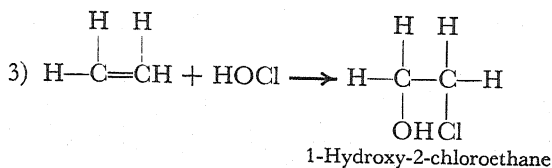
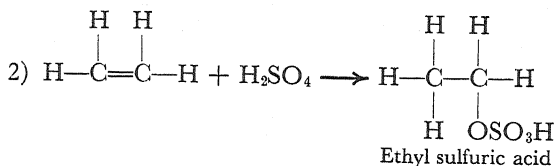
According to the I.U.C. system, these compounds are named in the same fashion that the paraffins are named. There is the added necessity in this series of designating the double bond and showing just where it is located in the molecule. The ending “-ene” indicates a double bond, and if there are several places where it might occur in the molecule, a number is placed after it (or before it) to indicate to which carbon it is attached. Only one carbon is indicated since the double bond must be attached also to the next carbon in the chain. If the double bond is between the 2 carbon and the 3 carbon in a chain, the ending for the name of the compound will be “-ene 2.” The smaller number is always used. Thus, “-ene 1” means a double bond between the 1 and 2 carbons, while “-ene 3” means a double bond between the 3 and 4 carbons.

In daily life, you are more likely to hear the common or old-fashioned name for these compounds.

The double bond is a chemically active bond and will add many small molecules to form new compounds. The double bond makes the members of the olefin series reactive rather than inert as the paraffins are. Ethylene (ethene) will be used as an example of some addition reactions. Other members of the series will react in a similar manner.

A. Addition reactions:



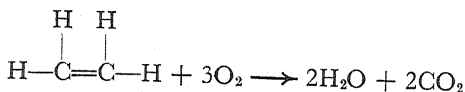
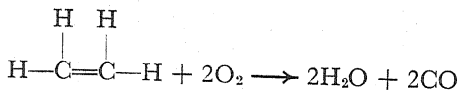
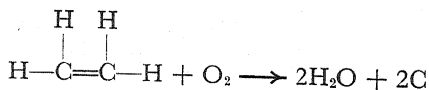


An addition reaction or one in which a molecule adds to another, is a reaction in which two molecules combine to produce just one new molecule. The products in the addition reactions above are named as derivatives of ethane, since they are saturated; they do not have a double bond.

Bromine and iodine will react with an olefin to add to the double bond in the same manner that chlorine adds to ethylene, but they are slower and sometimes require the presence of sunlight.

B. Oxidation with air.

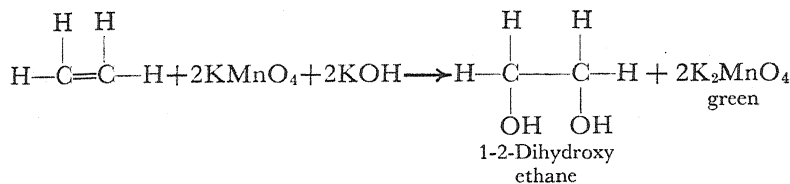
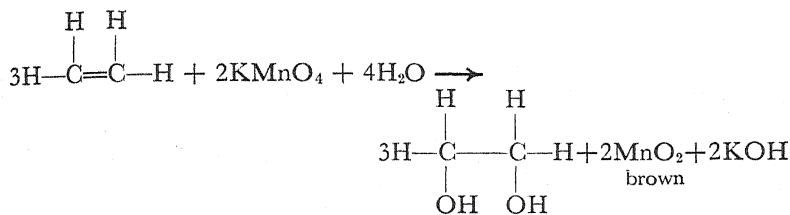
The members of the olefin series will burn in air by reacting with oxygen. The products will be water and carbon, carbon monoxide, or carbon dioxide according to the amount of oxygen available. If there is a large supply of oxygen available in an efficient burner, for example, the product is always water and carbon dioxide.



C. Oxidation with permanganate.

Most olefins are readily oxidized by permanganates. The permanganate is either reduced to brown manganese dioxide,

MnO_2 , or to green manganate, such as potassium manganate, K_2MnO_4 . The sharp change in color from a purple solution to a dark brown precipitate or to a green solution is so marked that this reaction is used as a test for a double bond. The olefin is oxidized to a compound where one hydroxyl group is attached to each carbon which has held the double bond. This product is called a dialcohol.



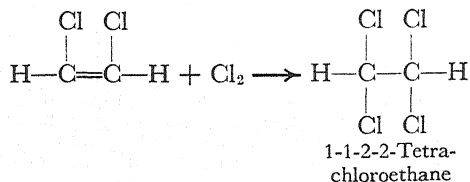
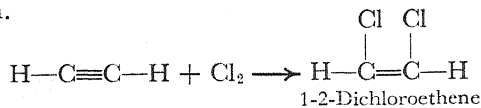
Acetylenes or Alkynes

The acetylenes have the general formula $\text{C}_n\text{H}_{2n-2}$. Each member of the series contains two carbons in the chain, which share six electrons between them, or a *triple bond*. Acetylene, the first member of the series, is a typical example:



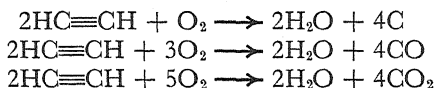
The triple bond is similar to the double bond in that it is chemically reactive, but it will add *two* small molecules instead of one.

A. Addition.



B. Oxidation.

The members of the acetylene family will also burn in air. They, too, produce water and either carbon, carbon monoxide, or carbon dioxide, depending on the supply of oxygen.



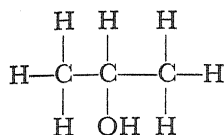
ALCOHOLS

Alcohols are organic compounds which contain an oxygen in a hydroxyl group, —OH , as well as carbon and hydrogen. They are, of course, not hydrocarbons, but a new class of compounds. The hydroxyl group is chemically active and gives the alcohols most of their chemical properties. This hydroxyl group is called the *functional group* of the alcohols since it regulates the way they function in chemical reactions.

The general formula for the alcohols is $\text{C}_n\text{H}_{2n+1}\text{OH}$. The $\text{C}_n\text{H}_{2n+1}$ is an organic radical — a methyl, ethyl, propyl, or related group. Sometimes the type formula for the alcohols is written ROH , where R stands for the organic radical. This formula is sometimes more useful, since it emphasizes the functional group.

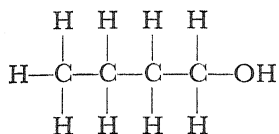
Common Alcohols

	<i>I.U.C. Name</i>	<i>Common Name</i>
$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	Methanol	Methyl alcohol
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	Ethanol	Ethyl alcohol
$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{OH} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	Propanol-1	Propyl alcohol



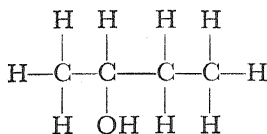
Propanol-2

Isopropyl alcohol



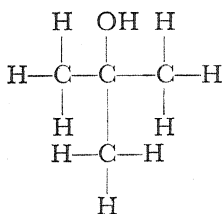
Butanol-1

Normal butyl alcohol



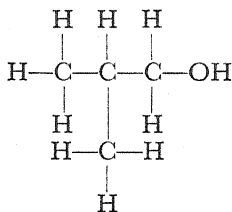
Butanol-2

Secondary butyl alcohol



2-Methyl propanol-2

Tertiary butyl alcohol



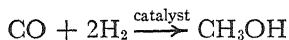
2-Methyl propanol-1

Isobutyl alcohol

The International Union of Chemistry names for the alcohols follow the same rules which have already been studied. The hydroxyl group is designated by the ending “-ol” and, where there is more than one possible place of attachment, the number which follows shows to which carbon in the chain it is attached. The “-an” which follows the root of the name indicates that the compound is saturated. Thus the name “butanol” shows from “but-” that there are four carbons in a chain; from “-an-” that it is saturated; and from “-ol” that it contains a hydroxyl group. You will wish to use the common names.

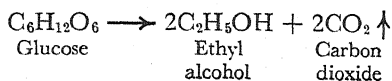
Methyl alcohol is the compound which you know as "wood alcohol." It is a colorless liquid with a characteristic odor and a boiling point of 65° C. It acquired this name many years ago because it was produced at that time by the destructive distillation of wood. Wood is made up of a number of different large molecules which decompose into smaller ones when it is heated in a pot and does not burn. Some decomposition occurs when wood burns, but the products burn too. You see this series of reactions when spurts of flame shoot out of a burning log. Methyl alcohol is the alcohol which is formed in the destructive distillation of wood and is, therefore, called "wood alcohol."

Today, with the high price of wood, it is not economical to prepare methyl alcohol by this method. Almost all methyl alcohol is prepared by a catalytic reaction of carbon monoxide and hydrogen.

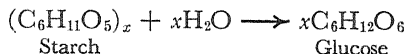


Methyl alcohol has many uses as a solvent, an antifreeze, and in the synthesis of numerous compounds. The limitations of its use are its fairly high toxicity. You have all read of deaths due to the use of methyl alcohol in beverages. It is poisonous not only when ingested, but also when it is inhaled or rubbed on the skin in fair amounts.

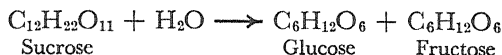
Ethyl alcohol is the compound which is called "grain alcohol" or "spirits." It, too, is a colorless liquid, but it boils at 760 millimeters at 78° C. It has been produced for centuries by the fermentation of glucose. Yeast cells are widely distributed in nature, and when they fall into a moist medium which contains the nutrients they need for life, they multiply rapidly. One of the nutrients which they need is glucose. Most fruits and many vegetables contain glucose, and when their skin is broken, the yeast cells begin to grow. The changes which these microorganisms bring about in glucose follow a long series of reactions. For most steps in the reaction chain, an enzyme or an enzyme system is used as the catalyst. The overall reaction is:



Other carbohydrates are sometimes used in the production of ethyl alcohol by fermentation. Starches from corn, wheat, and potatoes are changed to glucose by natural enzymes.



Sucrose, another carbohydrate, is enzymatically transformed to glucose and fructose.



The residues from the crystallization of sugar, either from cane or beets, contain the sugar sucrose, along with many other strongly flavored substances. This is "black strap molasses." The carbohydrate is available for fermentation to ethyl alcohol.

Commercially the fermentation process continues rapidly until the concentration of alcohol reaches 6 to 10 per cent. Then the growth of the yeast slows, and little additional alcohol is produced. The fermented mixture is distilled, and water and alcohol pass over in a mixture of 95 per cent alcohol and 5 per cent water which is ordinary industrial alcohol. In order to remove the last 5 per cent of water, it is necessary to treat the solution with a compound which will react with the water, or add another substance which will change the characteristics of the boiling mixture. Calcium oxide is commonly used in the laboratory to prepare pure dry alcohol. It reacts with water to form calcium hydroxide, which does not decompose at the boiling point of alcohol.



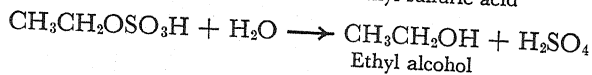
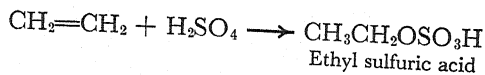
Industrial alcohol is treated with crude calcium oxide, the mixture warmed for a time, and then distilled. Pure dry ethyl alcohol distils over. This is called "absolute alcohol."

Since ethyl alcohol is the "stimulant" in alcoholic beverages, there is a high federal tax on ethyl alcohol. If it is made unsafe or unfit for drinking, it may be tax free. The United States government has a number of formulas for preparing "denatured alcohol" which are acceptable for use without taxation. Some contain methyl alcohol, others contain strong smelling compounds. None of the contaminants added to prevent the use of

the solution as a beverage can be easily removed. "Denatured alcohol" is 95 per cent ethyl alcohol, to which have been added other substances prescribed by the federal government to make the solution unfit for drinking.

Although ethyl alcohol has been known as a stimulant for centuries, it is actually a depressant. It is the brain and nervous tissues of the body which are affected by the presence of alcohol in the blood stream. When small amounts of alcohol are ingested, the cortex of the cerebrum is first affected. This is the highest part of the brain — the part concerned with judgments, inhibitions, and tensions. As the quantity of alcohol ingested increases, other sections of the brain show decrease in function. All tests of behavior, whether simple physical operations like placing nuts on bolts, or simple mental problems such as adding columns of figures, show that alcohol causes a decrease in performance. Probably the feeling of relaxation which some people experience from small quantities of alcohol is caused by a depression of their inhibitions. There is no demonstrable change in the structure of tissue exposed to alcohol in the blood stream. The devastating changes which occur in chronic alcoholism are now believed to be nutritional and a secondary effect of the alcohol. In chronic alcoholism, the diet is sometimes strikingly poor for long periods of time and deficiency disorders develop. (For an authoritative discussion of the whole problem of alcohol, see *Alcohol, Science and Society*, Yale Summer School of Alcohol Studies, 1945, Yale University Press.)

Ethyl alcohol and some of the higher alcohols are manufactured from olefins as well as produced by fermentation. Ethylene will react with sulfuric acid to produce ethyl sulfuric acid which hydrolyzes with water to form the alcohol.



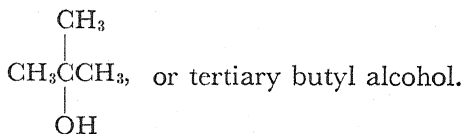
Some of the other alcohols are produced by fermentation reactions of other microorganisms than common yeast.

Alcohols are classified on the basis of the state of the carbon to which the hydroxyl group is attached, as *primary*, *secondary*, or *tertiary* alcohols. A primary alcohol is one in which the hydroxyl

group is attached to a carbon holding *one* other carbon. Ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$, is an example. Here the —OH is attached to the carbon which holds only the carbon of the methyl group. A secondary alcohol is one in which the hydroxyl group is attached to a carbon which holds *two* other carbon atoms. Isopropyl alcohol is a secondary alcohol, CH_3CHCH_3 . Notice



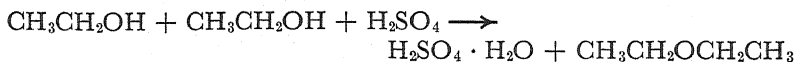
that the —OH group is attached to the center carbon which holds a carbon on each side of it. A tertiary alcohol is one in which the hydroxyl group is attached to a carbon which holds *three* other carbon atoms. An example is 2-methyl propanol-2,



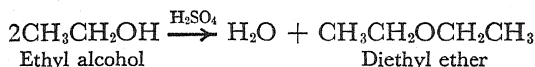
Reactions

Although all alcohols have the common functional hydroxyl group they do not react like hydroxides. The formulas for ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$, and for sodium hydroxide, NaOH , may appear similar, but the chemical properties of these two compounds are far different. The cause for this is in the occurrence of covalent bonds between the carbon, oxygen, and hydrogen in the ethyl alcohol and a lack of ionization and the occurrence of and electrovalent bond between the sodium and oxygen in sodium hydroxide and consequent ionization. A few of the reactions of alcohols will be studied.

1. Ether formation. Alcohols react at certain temperatures in the presence of dehydrating agents, such as sulfuric acid, to form one molecule of water from two molecules of the alcohol. The organic compound produced is called an *ether*.



Ordinarily we write the reaction:



This is a general reaction for alcohols.

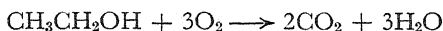
The *ethers* are named by naming the organic radicals and then adding "ether" for the oxygen. Thus "diethyl ether" has two ethyl groups attached to the oxygen. "Dimethyl ether" is a compound in which two methyl groups are attached to the oxygen.

Mixed ethers occur in which the organic radicals are different. Thus, methyl ethyl ether is known. But these mixed ethers cannot be prepared by the reaction given here. If a mixture of ethyl alcohol, methyl alcohol, and sulfuric acid were heated in the hope of producing methyl ethyl ether, only a small yield of that compound would be produced. Diethyl ether and dimethyl ether would also be formed in the reaction. Other reactions, which we shall not study, must be used to form mixed ethers.

Diethyl ether is a compound with which all of you are familiar. It is the most common substance used in general anesthesia, and many of you have had it administered for even minor surgery. When diethyl ether is inhaled, it produces a rapid anesthesia. It is quite safe, with a very low mortality rate. The chief objection to it is the common occurrence of nausea on recovery from the anesthesia. Divinyl ether, $\text{CH}_2=\text{CH}-\text{O}-\text{CH}=\text{CH}_2$, is said to have all the good qualities of diethyl ether and a much lower incidence of nausea. It is not widely used at present.

Ethers are used as solvents in many mixtures. You will use diethyl ether as a solvent in the laboratory for a number of compounds.

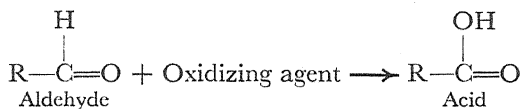
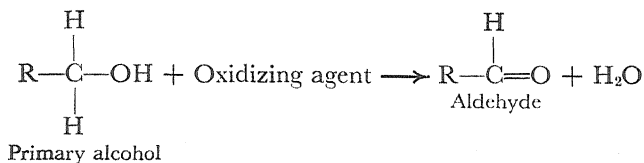
2. Oxidation. (a) Most alcohols will burn in air with the formation of water and either carbon, carbon monoxide, or carbon dioxide. Ethyl alcohol burns with a pale blue flame to form water and carbon dioxide.



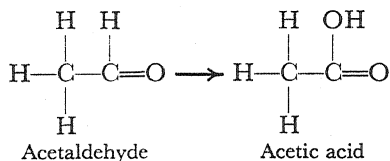
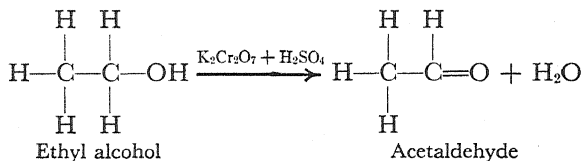
Most of you have never used an alcohol lamp, as your grandmothers did, to heat water for tea. But some of you have used "canned heat." Most of you have never seen brandy poured over plum pudding and ignited, but you know that it is traditional in some families. The fuel in the "canned heat" or in brandy is an alcohol. In the canned heat, it is usually methyl or isopropyl alcohol, while in brandy it is ethyl alcohol.

(b) When alcohols are warmed with oxidizing agents, such as potassium dichromate and sulfuric acid, or potassium permanganate, many are partially oxidized. A primary alcohol is oxi-

dized to an aldehyde, and if the aldehyde is not removed from the reaction mixture, it will be oxidized to an acid. This is shown by a general equation:

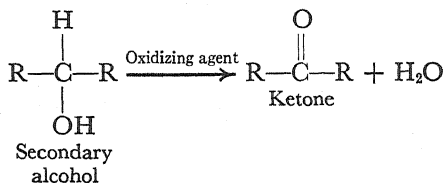


If a primary alcohol, such as ethyl alcohol, is slowly added to a warm mixture of potassium dichromate and sulfuric acid and the product is distilled off as it is formed, acetaldehyde will be produced. If the apparatus is arranged so that the vapors return to the flask (reflux condensor), acetic acid will be formed.

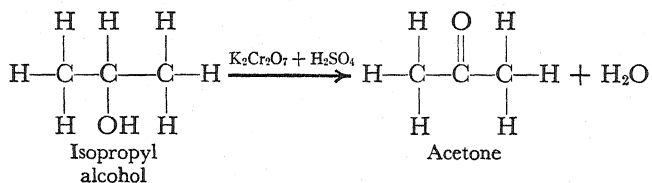


You will notice that the hydroxyl, —OH, group and a hydrogen on the alcoholic carbon have been replaced by an oxygen in the aldehyde. Since the oxygen has a valence of two, it replaces these two groups. The hydrogens on carbons in the molecule which do not hold alcoholic groups are not oxidized. Thus, when butyl alcohol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, is oxidized, it is the hydrogen and hydroxyl on the last carbon (the alcoholic carbon) which are replaced by an oxygen. The other hydrogens are not affected.

Secondary alcohols are oxidized by these agents to ketones. The general reaction is:

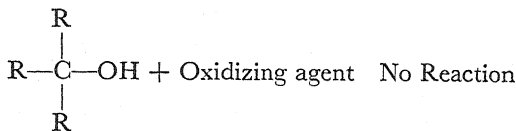


An example of a secondary alcohol is isopropyl alcohol, $\text{CH}_3\text{CHOHCH}_3$.



The oxidizing agent is reduced. In the case of dichromate, the products are potassium sulfate and chromium sulfate. The equation is not balanced so that attention is focused on the change in the organic molecules.

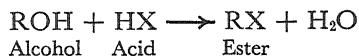
Tertiary alcohols do not possess a carbon holding a hydrogen as well as a hydroxyl, and they are consequently not easily oxidized. If the conditions of the reaction are such that any reaction will occur, the molecule is torn to pieces and a number of smaller molecules are produced. But under the same conditions by which primary alcohols are oxidized to aldehydes and then to acids and by which secondary alcohols are oxidized to ketones, no reaction occurs with tertiary alcohols.



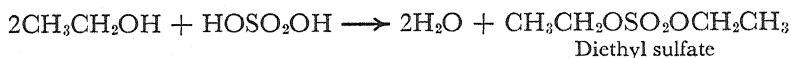
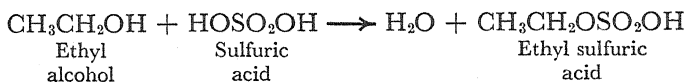
Three new classes of compounds have been introduced here which are produced from alcoholic oxidation — aldehydes, acids, and ketones. They will be studied in greater detail later.

3. Ester formation. Alcohols react with acids to form esters. Usually it is necessary to warm the mixture and add some sort

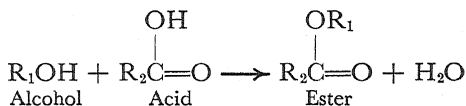
of catalyst. Sulfuric acid is a common one. Alcohols will react with both inorganic and organic acids.



For example, ethyl alcohol will react with sulfuric acid to form either ethyl sulfuric acid or diethyl sulfate. Other alcohols will show similar reactions.



Organic acids have the general formula, $\text{RC}=\text{O}$ and they react with alcohols according to the following general reaction:



Ester formation will be studied again under organic acids.

ACIDS

In your daily life you have encountered a few organic acids, which you probably know by name. Acetic acid is the substance which makes vinegar sour, while oxalic acid is in rhubarb, and citric acid is present in lemons and oranges. The functional group which gives acid properties to these compounds is the



carboxyl group, $\text{—C}=\text{O}$. This group produces some hydrogen ions and is, therefore, acidic. There are other groups which occur in some organic compounds which are acidic, but it is the carboxyl group which is most common. The general formula



for these organic acids is $\text{RC}=\text{O}$ or $\text{C}_n\text{H}_{2n+1}\text{C}=\text{O}$.

Some of the rather high molecular weight acids of this homologous series occur in fats and the series is, therefore, known as the saturated fatty acid series.

Saturated Fatty Acid Series

		<i>I.U.C. Name</i>	<i>Common Name</i>
HCOOH	$\begin{array}{c} \text{OH} \\ \\ \text{H}-\text{C}=\text{O} \end{array}$	Methanoic acid	Formic acid
CH_3COOH	$\begin{array}{c} \text{H} \quad \text{OH} \\ \quad \\ \text{H}-\text{C}-\text{C}=\text{O} \\ \\ \text{H} \end{array}$	Ethanoic acid	Acetic acid
$\text{CH}_3\text{CH}_2\text{COOH}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{OH} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}=\text{O} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	Propanoic acid	Propionic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{OH} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}=\text{O} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	Butanoic acid	Butyric acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{OH} \\ \quad \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}=\text{O} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	Pentanoic acid	Valeric acid

The common names are the names which you will use for these acids. Some of these compounds have been known for centuries and were named long ago from their source. There is mention in the Old Testament of vinegar, and when the compound which accounts for its sourness was isolated, it was given a name which means "sour." The Latin word for vinegar is "acetum" and that for sour is "acidus," but both have the same root. Formic acid was prepared in alchemical days by distilling red ants. The Latin word for ants is "formica" and "formic acid" means literally "acid from ants." Butyric acid was first isolated from butter, and this fact accounts for the name of the acid and the use of the root "but-" to mean four carbons.

The I.U.C. names follow the same rules for naming that were used for the hydrocarbons. The root of the name indicates the

number of carbons in the longest carbon chain and the ending “-anoic” indicates that the chain is saturated and terminates in



a carboxyl group, —C=O .

Branched chain acids are known, but you will not encounter many of them. They are named easily by using the I.U.C.

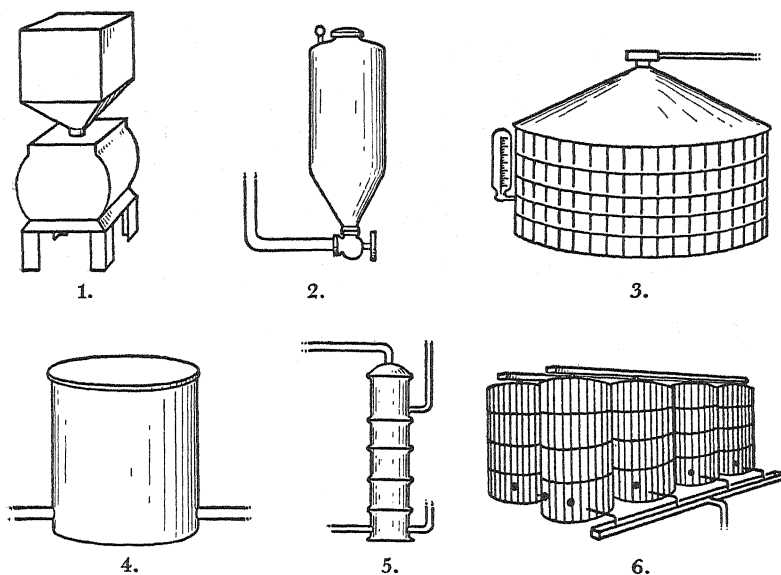


Fig. 22-8. Manufacture of vinegar. Corn and rye are (1) passed through a grinder and (2) steamed in a pressure cooker. (3) Water and sprouted barley are added in a mash tank to change starches into sugar. (4) Yeast in the fermentation tanks changes sugar to alcohol which is (5) removed by distillation. (6) The alcohol trickles over beechwood shavings, where a microorganism changes alcohol to acetic acid.

system of numbering the carbon chain and indicating to which carbon a group is attached.

Organic compounds which contain carboxyl groups are capable of ionizing weakly in water solutions. The high molecular weight acids are not soluble in water, but they undergo chemical reactions which indicate that the chemical properties of the carboxyl group are similar to those of the soluble members

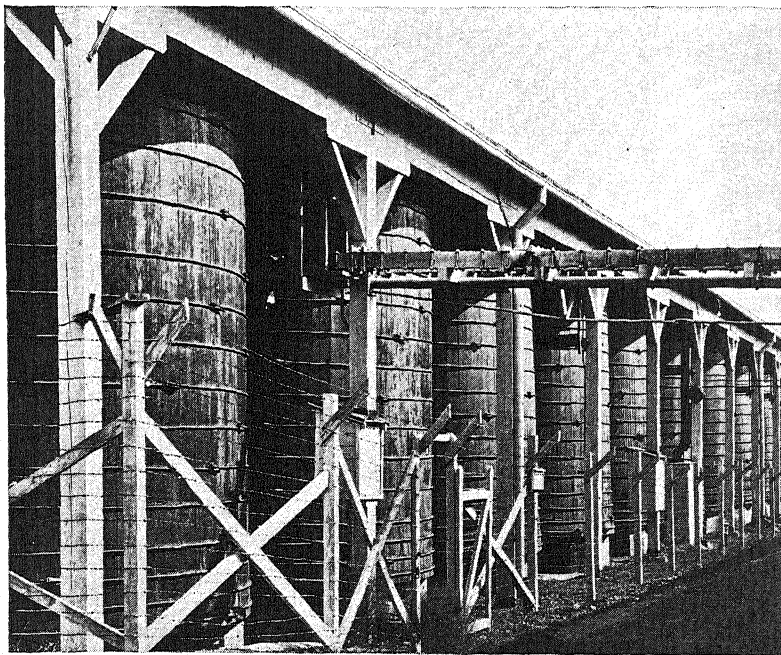
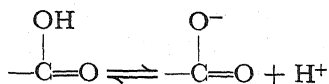
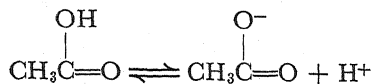


Fig. 22-9. Storage tanks for cider vinegar. (Courtesy of H. J. Heinz Co., Pittsburgh, Pa.)

of the series. The ionization consists of a loss of the hydrogen of the carboxyl group.



For acetic acid the ionic equation is:



The reaction is reversible; the hydrogen ion continually associates with the organic ion. A dynamic equilibrium exists. The extent of ionization is very small. A 0.1 normal solution of acetic acid only ionizes 1.3 per cent at 25° C. The extent of ionization varies with the length of the carbon chain. It decreases as the molecular weight increases.

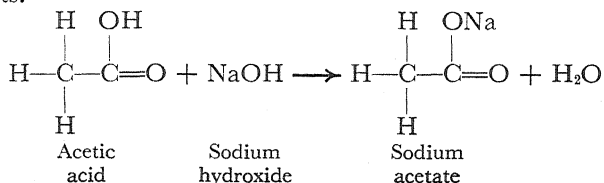
Formic acid is a colorless liquid at room temperature, with a boiling point of 100.5°C . at 760 millimeters pressure. Acetic acid is likewise a colorless liquid at room temperature, with a melting point of 16.7° and a boiling point of 118.1°C . at 760 millimeters pressure. Pure acetic acid is called "glacial acetic acid" because it freezes to a solid in cold laboratories. Here in the United States where laboratories are in very warm buildings glacial acetic acid is seldom seen as a solid.

Reactions

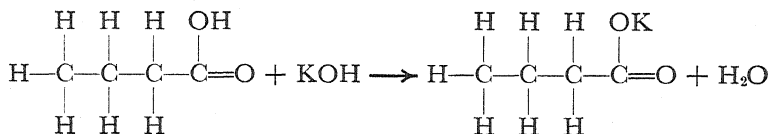
1. Salt formation. Organic acids react with hydroxides to form salts. The metallic ion of the hydroxide replaces the hydrogen of the carboxyl group.



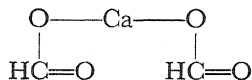
You are familiar with the reaction of acetic acid and sodium hydroxide. Here are the structural formulas for the reactants and products.



Butyric acid and potassium hydroxide form potassium butyrate and water.



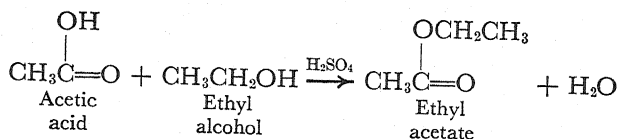
A base such as calcium hydroxide, in which the metallic ion has a valence of two, will react with two molecules of the organic acid. Calcium formate will have the following structure:



Salts are named in the same way that inorganic salts are named. The name of the metallic ion is given first, and this is followed

by the root of the name of the acid plus "-ate" in place of the "-ic." Thus we have "formate," "acetate," "propionate."

2. Ester formation. Alcohols react with acids to form esters and water. This reaction, on paper, looks very much like the reaction of an acid and a hydroxide. Actually it is far different. The difference between ionic and nonionic reactions is clearly demonstrated. Organic acids react rapidly with hydroxides to form salts, but very slowly with alcohols. The mixture of acid and alcohol must be heated in order to speed up the reaction and a catalyst must be used. While the product of the first reaction, a salt, is highly ionized, an ester shows no ionization at all.



Esters are named like salts despite their great difference in properties. The name of the radical derived from the alcohol is given in place of the metallic ion, and the name of the "-ic" acid is changed to "-ate."

Low molecular weight esters are colorless liquids with pleasant fruity or flower-like odors. Many are used as solvents for lacquers and other materials. You will recognize the odor of methyl acetate in some nail polishes. Other esters are used in flavorings and perfumes. Some occur naturally in the essential oils of fruits and flowers and give them their characteristic odors and flavors. Not all of the perfume of fruits and flowers is caused by esters, but they are one of the important groups of compounds.

ALDEHYDES

Aldehydes are a homologous series of organic compounds with

H
|
—C=O

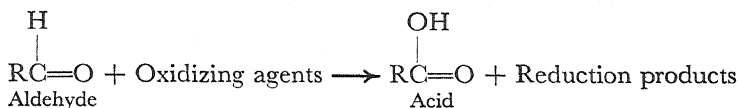
the functional group. They are named commonly for the acids which they readily form on oxidation. (The I.U.C. name follows the rule of naming the longest carbon chain and the radicals attached to it and adding the ending "-anal" to

indicate an aldehyde. You will seldom hear these names.) The root of the name of the acid is given and "aldehyde" is added to it.

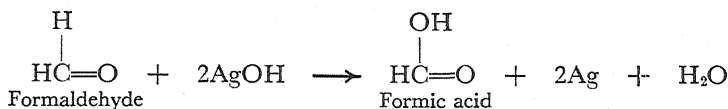
<i>Aldehyde</i>	<i>I.U.C. Name</i>	<i>Common Name</i>
$\begin{array}{c} \text{H} \\ \\ \text{HC}=\text{O} \end{array}$	Methanal	Formaldehyde
$\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{C}=\text{O} \end{array}$	Ethanal	Acetaldehyde
$\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{CH}_2\text{C}=\text{O} \end{array}$	Propanal	Propionaldehyde
$\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{C}=\text{O} \end{array}$	Butanal	Butyraldehyde

Aldehydes are very reactive compounds. It is the functional

group, $\begin{array}{c} \text{H} \\ | \\ \text{C}=\text{O} \end{array}$, which participates in the reactions. These reactions will not be studied except for the one of oxidation, which has already been mentioned. When aldehydes are treated with mild oxidizing agents they readily produce acids. The general formula for the reaction is:

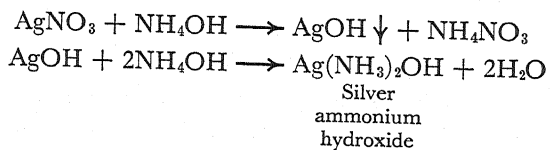


The hydrogen of the aldehyde group is readily oxidized to a hydroxyl group. For example:



The ease with which aldehydes are oxidized is so characteristic that the reaction with silver hydroxide is sometimes used to distinguish aldehydes from other compounds. This is called Tollens' test, or the silver mirror test.

A dilute solution of silver nitrate is treated with dilute ammonium hydroxide until the brown precipitate just dissolves. The silver nitrate first reacts with the ammonium hydroxide to form a precipitate of silver hydroxide. This then dissolves when more ammonium hydroxide is added to form a complex silver compound.



When the solution of silver ammonium hydroxide is treated with an aldehyde, free silver is formed. If the test tube or flask in which the reaction takes place is very clean, and if the solutions are very dilute and the mixture is gently warmed, the silver precipitates on the walls of the vessel as a shiny mirror. The

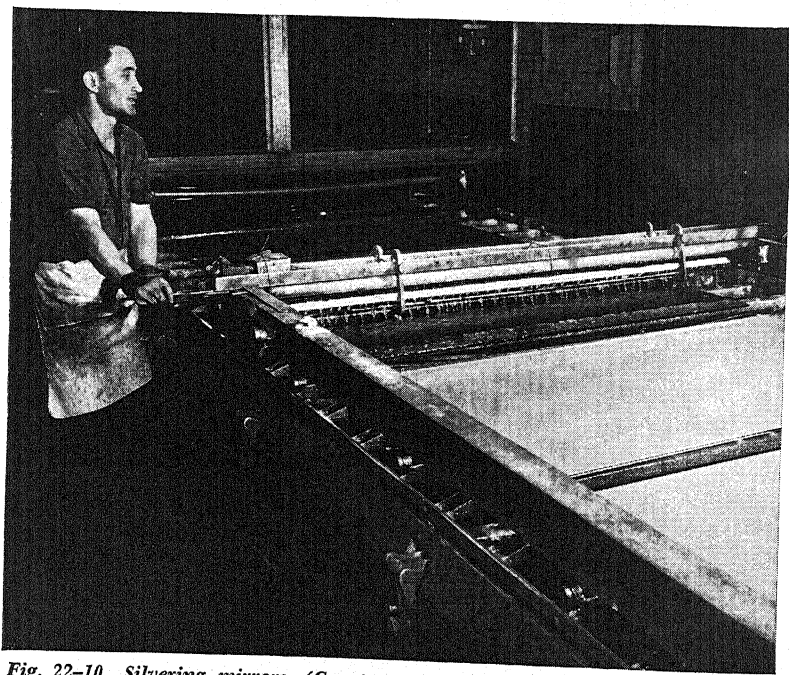
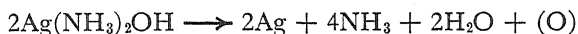


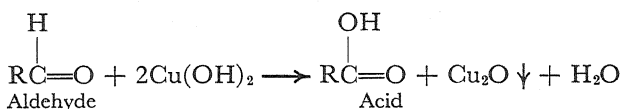
Fig. 22-10. Silvering mirrors. (Courtesy of Pittsburgh Plate Glass Company.)

reaction actually takes place between the aldehyde and the silver ammonium hydroxide.



The oxygen designated in the equation in parentheses is not formed unless it can be directly transferred to the aldehyde. The equation given above, in which the reactant was given as silver hydroxide, shows the trend of the reaction, but it is not strictly true.

Aldehydes also react with solutions of copper salts. Fehling's solution is one of these reagents. It is composed of copper sulfate, sodium hydroxide, and sodium potassium tartrate. These three compounds react to form a complex tartrate. For the purposes of the test, the reagent may be considered a solution of cupric hydroxide. In the presence of aldehydes, the cupric hydroxide is reduced to cuprous oxide and the aldehyde is oxidized to an acid. Since the cuprous oxide is a bright yellow, orange, or red precipitate, depending on the conditions during which it is formed, it is very easily seen and therefore a good test for even small quantities of aldehyde.



Industrially formaldehyde is the most important aldehyde. At room temperature it is a gas, since its boiling point is 21°C . A 40 per cent solution is sold under the name "formalin." Large quantities are used in the formation of formaldehyde resins, which are plastics. The oldest plastic is Bakelite, a formaldehyde phenol resin. It is also used in the preservation of biological specimens and as an antiseptic. Acetaldehyde is used in many synthetic reactions.

KETONES

Ketones are a homologous series of organic compounds with a functional group, >C=O , attached to two carbon radicals. The simplest ketone is acetone, $\text{CH}_3\text{C}=\text{OCH}_3$. The common

names for ketones give the names of the two carbon radicals attached to the carbonyl, >C=O , group and then add "ketone." By this system, acetone is "dimethyl ketone."

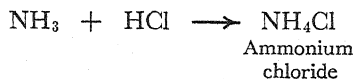
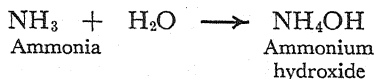
Ketones are produced by the oxidation of secondary alcohols with oxidizing agents such as dichromates and permanganates.

Ketones are not readily oxidized. If the conditions of oxidation are stringent enough, the carbon chain will be broken and smaller molecules will be produced. Ketones may be readily differentiated from aldehydes by this resistance to oxidation. Ketones do not react with either Tollens' reagent or Fehling's solution.

Acetone is the most important ketone industrially. It is widely used as a solvent for a great variety of organic compounds. It is a colorless liquid with a sweet, characteristic odor.

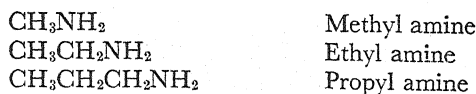
AMINES

Amines are organic compounds which are derivatives of ammonia. They contain a nitrogen atom with a covalence of three or five, such as the nitrogen has in ammonia. You remember how ammonia reacts with water or with acids.



The amines react as if they were derivatives of ammonia, in which one, two, or three of the hydrogens have been substituted with organic radicals. The compounds in which one hydrogen is substituted are called *primary amines*; those with two hydrogens substituted are called *secondary amines*; and those with three hydrogens substituted are called *tertiary amines*.

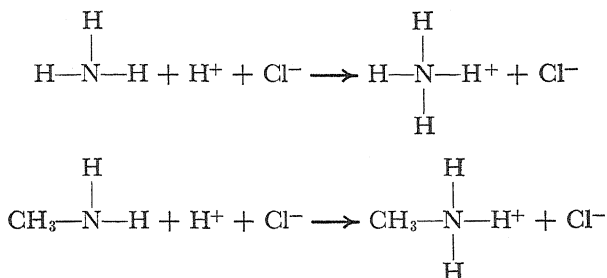
Primary Amines



Secondary Amines*Tertiary Amines*

This chart gives you an idea of the simple members of the amines. You see that an organic radical like a methyl group may be substituted for one, two, or three hydrogens to give either methyl amine, dimethyl amine, or trimethyl amine. Mixed amines in which the organic radicals are unlike also occur.

The amines are mildly basic compounds since they will combine with acids such as hydrochloric acid. Structurally the reaction of ammonia and hydrochloric acid consists of the binding of the hydrogen ion of the acid to the ammonia molecule to form an ammonium ion. The amines react in a similar fashion.



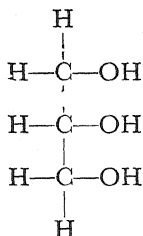
The product is a derivative of ammonium chloride. In organic chemistry it is usually called, however, an amine hydrochloride. Thus the salt produced from the reaction of methyl amine and hydrochloric acid is called methyl amine hydrochloride and is usually written $\text{CH}_3\text{NH}_2 \cdot \text{HCl}$. The $-\text{NH}_2$ group is called the amino group.

POLYFUNCTIONAL COMPOUNDS

So far compounds which have only one functional group — an alcoholic hydroxyl, an aldehyde, a carboxyl, or an amino group have been studied. There are many compounds which contain more than one functional group. Sometimes the functional groups may be the same, sometimes they are different. A

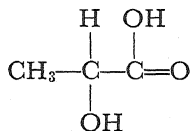
few of the compounds of interest to you will be given. Try to pick out the functional groups and decide to which series the compound belongs.

Glycerol is the alcohol portion of the esters which occur in fats. It is formed when these esters are hydrolyzed to produce the alcohol glycerol and the acids. It is known on the market as "glycerine." It has the formula



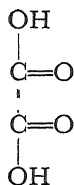
It is widely used for keeping tobacco moist, as a dressing for leather, in hand lotions, as an antifreeze, and in inks, and for the preparation of glyceryl trinitrate, the explosive in dynamite.

Lactic acid occurs in small quantities in muscle and in sour milk. Its formula is



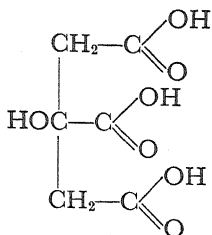
and it is, therefore, both an acid and an alcohol. It is a syrupy liquid and is used in dyeing and for the synthesis of some compounds. It is the acid in sour milk which accounts for its acidity.

Oxalic acid occurs in rhubarb, in spinach, and in some other fruits and vegetables in small amounts. It has the formula

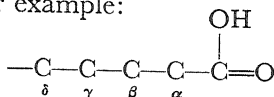


In other words, oxalic acid is a compound made up of two carboxyl groups.

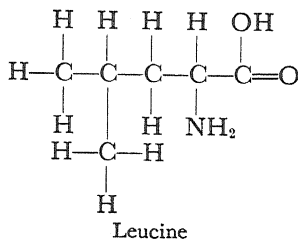
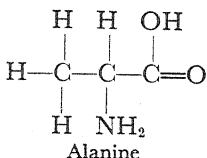
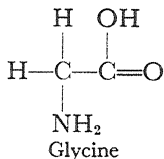
Citric acid is even more complicated, since it has four functional groups, three carboxyl groups and one alcoholic hydroxyl. It is widely distributed in nature in small amounts in fruits and vegetables.



The *amino acids* are important compounds which contain a carboxyl group and an amino group. All those which occur naturally have the amino group on the carbon next to the carboxyl group. One of the old methods for numbering the carbons in the chain of an acid is to start with the carbon NEXT to the carboxyl group and number them away from there by use of the Greek alphabet. It sounds complicated, but it is not. The first carbon is the alpha carbon, the next beta, then gamma, then delta, etc. For example:



Since the naturally occurring amino acids possess an amino group attached to the alpha carbon, they are called "alpha amino acids." They are formed on hydrolysis of protein. A few of the simple ones are given below. More will be studied when we come to proteins.

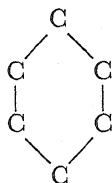


RING COMPOUNDS

It was pointed out on p. 336 that organic compounds occur, some of which have straight chains of carbon atoms, some with

branched chains, and some with rings. A brief glimpse will now be taken of some of the compounds which contain rings of carbon atoms.

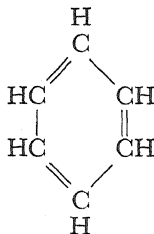
Carbon rings occur with four, five, six, or seven carbon atoms in the ring, and rarely with other numbers of carbon atoms. The most common number is six carbons in the benzene or phenyl ring.



In the aromatics there are compounds which are hydrocarbons, alcohols, aldehydes, ketones, acids, ethers, esters, and amines as there are in the chain or aliphatic compounds.

Benzene, C_6H_6

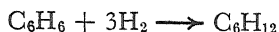
Benzene is a hydrocarbon with a very unusual type of unsaturation which is characteristic of these compounds. The molecular formula, C_6H_6 , suggests that this compound is highly unsaturated. Yet it does not react with bromine water or reduce potassium permanganate. These two reactions, you will remember, are characteristic of the olefins and acetylenes. The formula is commonly written either with three double bonds and the understanding that these are not olefinic double bonds



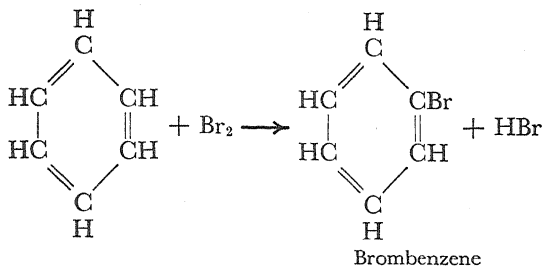
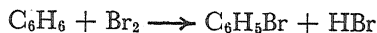
or as a hexagon with the understanding that a carbon and hydrogen are at each corner.



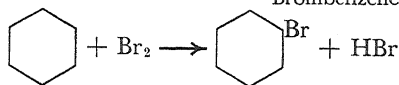
Benzene can be made to react with hydrogen to produce a compound, C_6H_{12} .



This reaction requires high temperatures and pressures and the presence of a catalyst. Ordinarily benzene reacts like a saturated compound and undergoes substitution reactions.

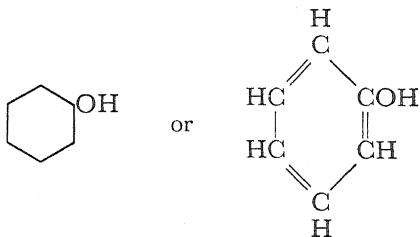


or

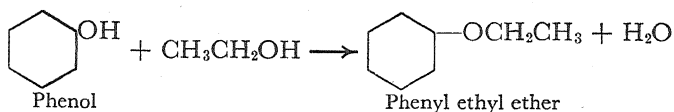


Benzene is sold under the trade name of "benzol." It is widely used as a starting material in synthetic chemistry and it is also a solvent for many compounds and mixtures.

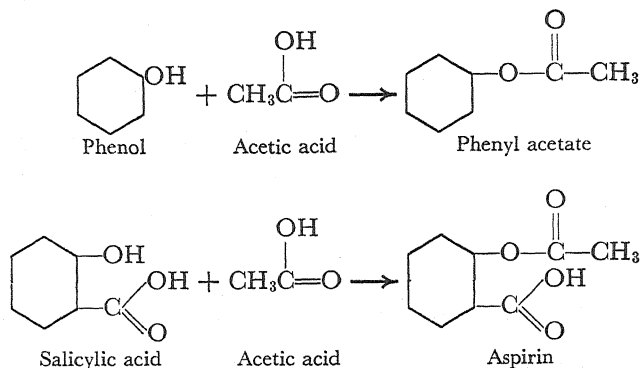
When one of the hydrogens on the benzene ring is substituted by a hydroxyl group, the compound is *phenol*.



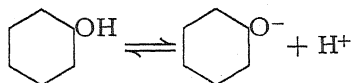
Phenol, and compounds similar to it which have a hydroxyl group directly attached to the ring, are alcohols. They react with other alcohols to form ethers.



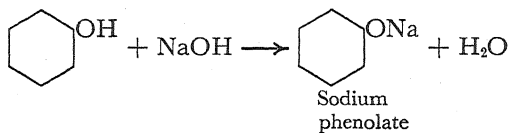
They react with acids to form esters.



The hydroxyl group attached directly to the benzene ring has a slight tendency to ionize. This means that it has weak acid properties.

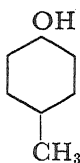
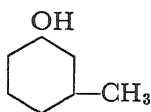
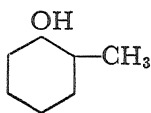


Phenol will neutralize sodium hydroxide. It is commonly called "carbolic acid."



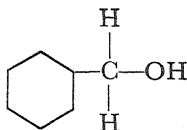
Phenol is used in large quantities for the production of formaldehyde-phenol resins. Bakelite was the first of these resins to be used widely. It is also used as an antiseptic.

The *phenol number* of an antiseptic is a measure of its ability to kill bacteria compared to phenol. Phenol is a fairly good antiseptic. The limitations to its use are the fact that it not only kills microorganisms, but also has a similar effect on body cells. It cannot be used in contact with the body. It is used in disinfecting pans, toilets, etc. The cresols, which contain a methyl group on the benzene ring as well as the hydroxyl group, are also widely used as disinfectants of this type.



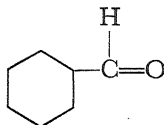
Cresols

Benzyl alcohol is a compound in which the hydroxyl group is not attached directly to the benzene ring, but instead is on the carbon which is not in the ring.



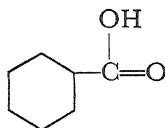
This compound acts as an alcohol and has none of the weakly acid properties of phenol. It is closely related in its chemical behavior to ethyl alcohol.

Benzaldehyde has chemical properties similar to the aliphatic aldehydes. It is a colorless liquid which turns yellow on standing.

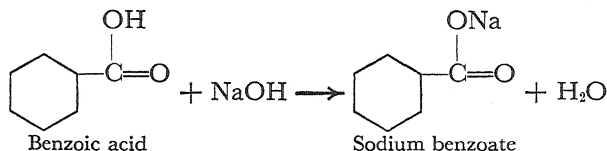


It has a pleasant odor of almonds and is used in flavorings and perfumes.

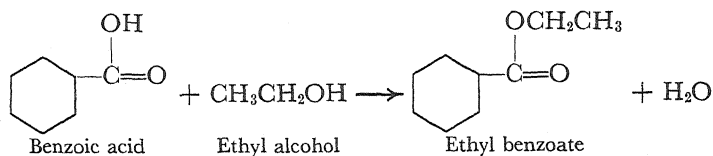
Benzoic acid is a white crystalline solid which is difficultly soluble in water, but which dissolves in sodium hydroxide.



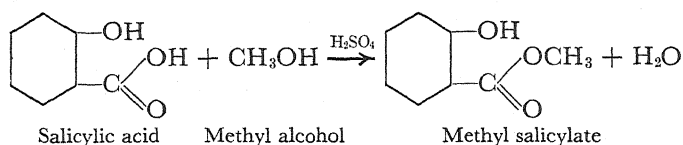
This is not surprising, since the carboxyl group has acidic properties in this compound, as it does in other organic compounds. The reaction is the following:



Benzoic acid acts as a typical acid and forms esters as well as salts.

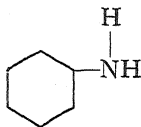


Other compounds which contain a carboxyl group attached to the benzene ring have chemical properties similar to benzoic acid. For example, salicylic acid will react with methyl alcohol, on warming a mixture in the presence of sulfuric acid, to form methyl salicylate.



This product is *oil of wintergreen* and has the sweet pleasant odor of wintergreen. It is used in flavorings and as a counter-irritant for relieving the pain of sprains and muscle strains.

Aniline is the simplest amine related to benzene. The nitrogen of the amino group is attached directly to the benzene ring.

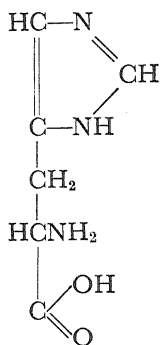


This compound and those related to it show reactions characteristic of amines. Aniline is used in large quantities in the production of synthetic chemicals. Many dyes are produced from aniline and are called the aniline dyes. Aniline itself is not a dye, but is simply the starting material in the preparation of these dyes.

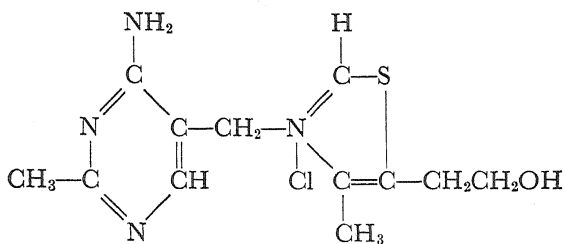
These few compounds should give you a glimpse of the large number of ring compounds. They cannot be studied in detail. You should recognize that these compounds have properties similar to those of the aliphatic series but that the properties are sometimes influenced by the presence of the benzene ring.

HETEROCYCLIC COMPOUNDS

The benzene ring is composed of six carbon atoms; in other words, the members of the ring are all alike. There are numerous compounds which have rings in which other elements occur. The most common elements, other than carbon, in these rings are oxygen, nitrogen, and sulfur. Such rings are called "heterocyclic." This means that there are different elements in the ring. There is not time to study these compounds, but a few examples of compounds which you will encounter are given to illustrate heterocyclic rings.



Histidine
One of the amino
acids of protein



Thiamine
Formerly vitamin B₁

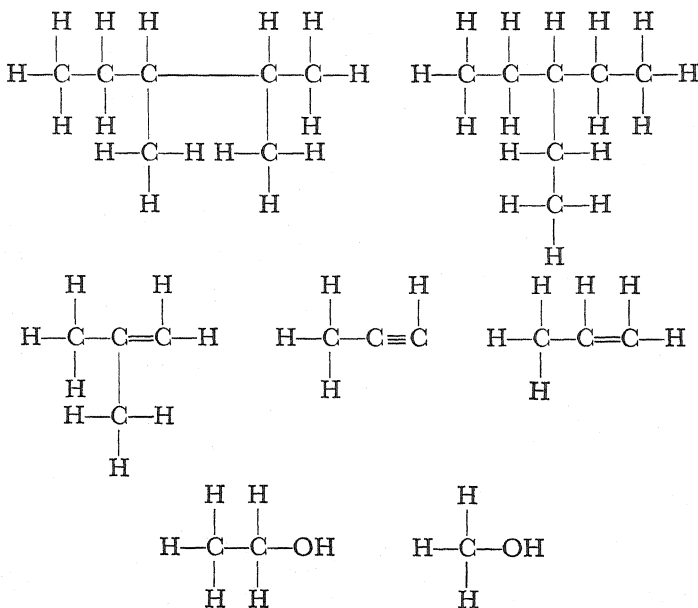
NEW TERMS

Isomerism, structural formula, hydrocarbon, aliphatic, aromatic, homologous series, general formula, paraffins or alkanes, olefines or alkenes, International Union of Chemistry, double bond, unsaturation, triple bond, functional group, alcohol, aldehyde, ether, ketone, carboxyl group, amine, amino group.

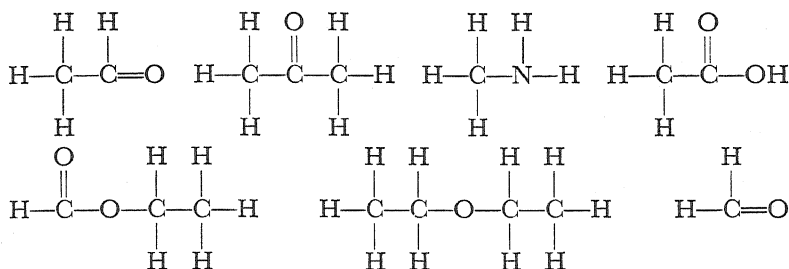
QUESTIONS

1. Why is organic chemistry a separate branch of chemistry?
2. What compounds comprise the field of organic chemistry?
3. Why was Wöhler's synthesis of urea of outstanding importance as far as the development of organic chemistry was concerned?
4. What are the general properties of organic compounds?

5. Name five materials in our daily life which are primarily mixtures of organic compounds. Name five compounds in our daily life which are organic compounds. (You need not give their chemical names.)
6. Calculate the empirical formula for an organic compound which contains 76.60 per cent carbon, 6.38 per cent hydrogen, and 17.02 per cent oxygen.
7. Calculate the empirical formula of a compound which contains 81.28 per cent carbon and 18.18 per cent hydrogen.
8. Calculate the molecular formula for a compound which has a molecular weight of 114 and contains 84.22 per cent carbon and 15.79 per cent hydrogen.
9. Calculate the molecular formula for a compound with a molecular weight of 52, containing 54.55 per cent carbon, 36.36 per cent oxygen, and 9.09 per cent hydrogen.
10. Carbon compounds are, for the most part, covalent compounds. By the use of diagrams, show the electronic structure of the following compounds: CCl_4 , CH_3CH_3 , CH_3OH .
11. Draw a tetrahedral carbon atom and explain the structure of CH_4 in three-dimensional space.
12. Give the rules of nomenclature for the paraffin or alkane series.
13. Name the following compounds:



14. Give the structural formulas for: propane, 2-methyl butane, 2-2-3-trimethyl butane, 3-ethyl pentane, 2-2-dimethyl propane.
15. Where do the paraffin or alkane hydrocarbons occur?
16. How is gasoline prepared? What is the "octane number"?
17. Show by a chemical reaction the difference between a double bond and a single bond. How many electrons are shared by two carbons which are joined by a double bond?
18. What part of the name distinguishes an olefin or alkene from a paraffin or alkane?
19. Give the structural formulas for the following compounds: ethylene, butene-1, butene-2, methyl propene, 2-2-dimethyl pentene-3.
20. Name the following compounds:



21. Give balanced equations using structural formulas for the following reactions:
 - a. Propene + bromine.
 - b. Ethylene + oxygen of air.
 - c. Ethane + oxygen of air.
 - d. Methane + chlorine.
 - e. Acetylene + bromine.
 - f. Ethylene + $\text{KMnO}_4 + \text{KOH}$.
22. How do primary, secondary, and tertiary alcohols differ structurally? What are the products, if any, of mild oxidation of primary, secondary, and tertiary alcohols?
23. What is the functional group of an alcohol?
24. Where does methyl alcohol occur? Ethyl alcohol?
25. Write balanced equations with structural formulas for the following reactions:
 - a. Ether formation from propyl alcohol.
 - b. Methyl alcohol + formic acid (H_2SO_4).
 - c. Ethyl alcohol + sulfuric acid.
 - d. Acetic acid + propyl alcohol.
26. Show by structural formula the oxidation of propyl alcohol to aldehyde to acid; of methyl alcohol. Name the compounds.

27. Show the ionization of propionic acid. Write the neutralization reaction of butyric acid and sodium hydroxide. How does the salt ionize?
28. Write structural formulas for the following compounds: sodium formate, calcium acetate, butyraldehyde, acetone, methyl propionate, diethyl ether, butyl acetate, ethyl formate.
29. Describe Tollens' test for an aldehyde and explain the reaction. What is the Fehling's solution test?
30. Give three examples of amines. Why do they neutralize acids? Write the structural formulas for the compounds which will be formed when the amines you named react with hydrochloric acid.
31. What is a polyfunctional compound? Give three examples.
32. What is a natural amino acid? Give examples.
33. Write structural formulas for the organic compounds formed in the following reactions:
 - a. Benzaldehyde + $\text{K}_2\text{Cr}_2\text{O}_7$.
 - b. Phenol + NaOH .
 - c. Acetic acid + salicylic acid.
 - d. Benzoic acid + methyl alcohol.
 - e. Aniline + HCl .

BIOCHEMISTRY

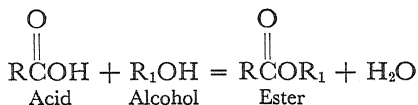
Lipides

CHEMISTRY OF THE MAJOR ORGANIC COMPOUNDS OF FOODS

Fats are one type of organic compounds included in the group known as lipides (sometimes called lipins, lipoids, or lipids). When foods and other biological materials are extracted in attempts to separate components with such organic solvents as ether, benzene, or chloroform, the lipides are dissolved. The lipides are differentiated from other organic substances by this solubility and by other chemical and physiological properties. They are defined (Bloor, 1925) as substances having the following properties:

1. Insolubility in water and solubility in fat solvents such as ether, benzene, chloroform.
2. Relationship to the fatty acids as esters, either actual or potential.
3. Utilization by living organisms.

Property 2 which states that they are *actual* or *potential* esters of fatty acids appears ambiguous. But if the types of compounds which are extracted by fat solvents from plant and animal tissues are surveyed you will readily understand what is meant. You will remember (1) that an ester is the product of an organic acid and an alcohol



and (2) that a fatty acid (or fat acid) is a straight-chain carbon acid, saturated or unsaturated, and usually with an even number of carbon atoms. The types of compounds included in the group, lipides, are all esters of fatty acid except the sterols. These are complex alcohols which in biological material such as blood, occur sometimes free and sometimes combined with fatty acids as esters.

The lipides include: A. Simple lipides

1) Simple esters of fatty acids

- a. Fats — esters of glycerol and fatty acids
- b. Waxes — esters of certain alcohols other than glycerol (high molecular weight, monohydric) such as sterols

B. Complex lipides

2) Complex esters of fatty acids

- a. Phospholipides — esters of fatty acids, phosphoric acid, an amine, and usually glycerol
- b. Galactolipides (cerebrosides) — esters of fatty acids, the sugar galactose, and the amine, sphingosine

3) Derived lipides

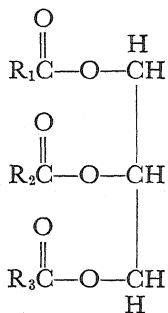
- a. Free fatty acids
- b. Sterols — high molecular weight alcohols with a complex condensed nucleus (phenanthrene)

Most attention will be confined to the fats since they are quite simple chemically and since the story of their function and fate in the animal body is a little more complete. It is not that the fats are more important than the phospholipides or sterols, for example. Indeed, the brain and nervous tissue is unusually rich in the complex lipides, and we find them distributed widely through the human body. But despite careful and extensive research, knowledge is still very fragmentary concerning these compounds. With the fats, too, there are many questions still unanswered, but knowledge is a little more complete.

FATS

Structure

Fats are esters of glycerol and fatty acids with the general structural formula:



All natural fats are mixtures of molecules, some containing small quantities of fat molecules in which the fatty acid is identical (tristearin, triolein, tripalmitin) and all containing large quantities of esters in which the acids in an individual molecule are not identical (mixed glycerides). Some of the common fatty acids which make up these esters are:

Stearic	
$C_{17}H_{35}COOH$	$CH_3(CH_2)_{15}CH_2COOH$
Palmitic	
$C_{16}H_{31}COOH$	$CH_3(CH_2)_{14}COOH$
Oleic	
$C_{17}H_{33}COOH$	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Linoleic	
$C_{17}H_{31}COOH$	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
Linolenic	
$C_{17}H_{29}COOH$	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$

Notice that they are all straight-chain acids; that they all contain an even number of carbon atoms (all 18 except palmitic which has 16); that stearic and palmitic are saturated while oleic, linoleic, and linolenic are unsaturated. Natural fats and oils vary slightly in their composition depending on environmental conditions of production. However the following table gives some indication of the variation between fats.

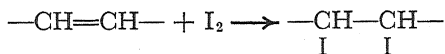
Percentage of Fatty Acids by Weight in Some Edible Fats and Oils *

		Corn	Cotton- seed	Olive	Leaf Lard	Beef Tallow	Mutton Tallow	Butter
Myristic	$C_{13}H_{27}COOH$	0%	1%	1%	1%	2%	2%	10%
Palmitic	$C_{16}H_{31}COOH$	6	21	9	28	32	34	30
Stearic	$C_{17}H_{35}COOH$	2	2	1	8	15	19	11
Arachidic	$C_{19}H_{39}COOH$	1	1	1	0	0	0	
Oleic	$C_{17}H_{33}COOH$	37	25	80	56	49	43	30
Linoleic	$C_{17}H_{31}COOH$	54	50	8	5	2	2	3
Butyric	C_4H_7COOH							3
Caproic	$C_6H_{11}COOH$							2
		100	100	100	98	100	100	99

* From Bailey, A. E., *The Chemistry and Technology of Food and Food Products*, edited by Jacobs, M. B., Vol. I, pp. 581-582. Copyright, 1944, by Interscience Publishers, Inc., New York.

Oils, fats which are liquid at room temperature because they have low melting points, have in general a greater amount of unsaturated fatty acids in their esters than do those fats which are solids at room temperature. This is demonstrated by the analyses presented in the table. It will be noted that the oils, corn, cottonseed and olive have a higher percentage of unsaturated acids, oleic and linoleic, than do the solid fats.

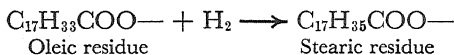
The amount of unsaturation in the fatty acid portion of the esters of fats is readily determined by dissolving the fat and adding to it a solution containing a known quantity of iodine, iodine monobromide, or iodine trichloride. The iodine adds to the double bonds of the unsaturated acids in the familiar fashion:



After a short time the excess iodine is determined, and the *iodine number* is expressed as the number of grams of iodine which will add to 100 grams of fat. The greater the unsaturation, the larger will be the iodine number.

Hydrogenation

Hydrogen will also add to the double bonds of the unsaturated acids combined in esters in oils if a suitable catalyst is present. As the fat becomes more saturated the melting point rises and a



product is obtained which is more appealing and more useful to the American housewife than oils. In 1947, 1103 million pounds of hydrogenated fats were produced. Most of this was vegetable fat from cottonseed, peanut, soybean, coconut, and palm oils. A small amount of animal fat such as lard and some fish oil is also used.

The hydrogenation is carried out by dissolving hydrogen in the liquid fat and then adding the finely divided nickel catalyst. The rate and amount of hydrogenation is carefully controlled so that the properties of the product may not vary. After hydrogenation, the fat is filtered, deodorized, and rapidly chilled to a

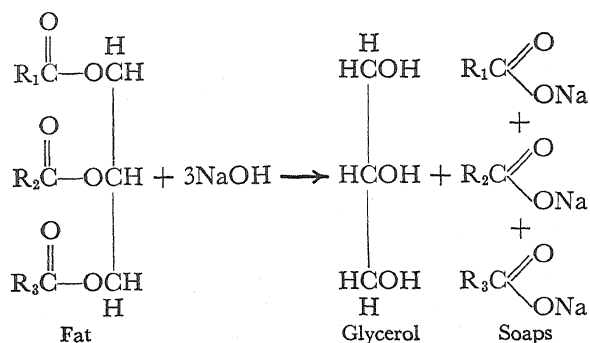
soft product. It is usually then emulsified with air to the extent of 6 to 15 per cent by volume, in order to impart a white appearance. Since 1934 the practice of adding monoglycerides to shortening has become widespread in the United States. These are called "high ratio" or "superglycerinated" shortenings and have the advantage of readily emulsifying with the aqueous ingredients of batters. Bailey says, "The high degree to which the fat may be dispersed and the consequent mechanical strength of the emulsion enable the baker to increase the liquid content of his cake doughs greatly without weakening them sufficiently to cause them to fall during the baking operation. This increase in the liquid content permits the use of higher ratios of sugar to flour and the consequent production of a sweeter cake."^{*}

Margarine manufacturers in the United States use hydrogenated mixtures of fats very widely. To the melted fats they add skim milk which has been inoculated with lactic acid and flavor-producing bacteria. The mixture is churned until it is fairly uniform and is then chilled. It is allowed to ripen for 12 to 24 hours, salt is added, and it is well blended. Margarine ordinarily consists of about 80 per cent fat, 17 per cent milk, and 3 per cent salt. The production of margarine in the United States has been restricted because of federal and state legislation. The ten cents per pound federal tax on yellow-colored margarine has been removed, but many states impose restrictions. During World War II with the limited quantity of butter the use and sale of margarine became more widespread. Most margarine sold in the United States is fortified with carotene (provitamin A). It has been many years since the author has seen a pound of margarine which had not been fortified.

Saponification

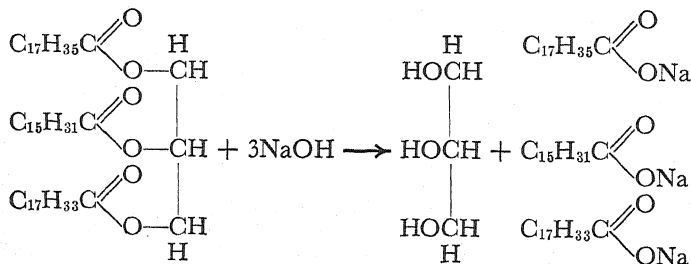
Since fats are esters, they are hydrolyzed with considerable ease. When the hydrolyzing agent is an alkali, the reaction is called a *saponification* since salts of the fatty acids, soaps, are produced.

^{*} Bailey, *The Chemistry and Technology of Food and Food Products*, edited by M. B. Jacobs, Vol. II, p. 713. Copyright, 1944, by Interscience Publishers, Inc., New York.



Commercial soap is made from a number of fats and oils by this simple reaction. The characteristics of the soap depend on the fatty acids present. Low-grade tallow obtained from cattle, horse, and sheep fat produce a firm soap which "dissolves" slowly. Crude coconut oil produces a firm soap which lathers readily and is used in the production of most household soaps. Palm oil from the flesh of the palm nut yields a hard soap. Olive oil is an expensive raw material, but produces a soap with the desirable quality of lathering readily in cool water. It is used to a limited extent in castile soaps. High-grade cottonseed, sesame, and corn oil are too expensive for use in soaps, but whale oil when it is available and cheap, is sometimes used. This oil has a fishy odor which is still present in the finished soap. The oil is, therefore, first hydrogenated and then deodorized before it is saponified. Gum rosin consisting mainly of abietic acid or its anhydride, a high molecular weight acid, is neutralized with Na_2CO_3 and added to yellow laundry soap. It increases the ease with which the soap lathers, although in large quantity it makes the soap sticky.

EXAMPLE:

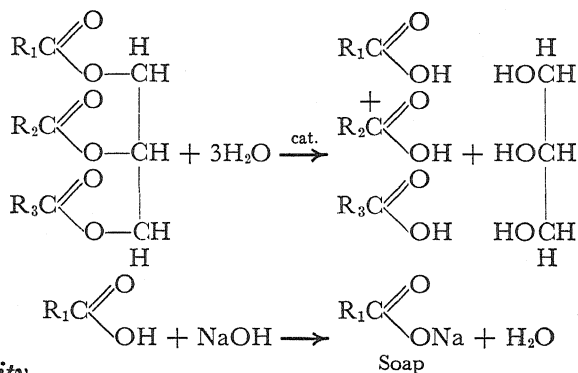


During the war years, when the war industries had first priority on the tallow and grease available, the soap industry had to depend more on such oils as soybean, palm, and coconut. The production of soaps during the first nine months of 1948 exceeded 1,945 million pounds (about 90 per cent reported) while liquid soap amounted to 2.38 million gallons.

In the commercial production of soap, melted fat is boiled with NaOH or KOH until saponification is complete. It is separated from the solution of glycerol and alkali by adding solid NaCl or a concentrated brine solution. Since soaps do not form a true solution, but rather a colloidal dispersion, they are precipitated in the presence of this high electrolyte concentration. This precipitation is repeated to further purify the soap. The glycerol and salt are recovered from the liquors.

All soap produced in the United States has some perfume added to it and frequently a coloring agent. ZnO or TiO₂ is frequently added to toilet soap to increase the whiteness. Soap beads or granules contain 20 to 40 per cent "builder," inorganic sodium salts with high pH. The action of soap as a detergent and of builders will be discussed in Chapter 32 on cleaning agents.

Some soap is produced by the Twichell method. Here fats are hydrolyzed with water at a high temperature and in the presence of a catalyst. The insoluble fatty acids separate and after filtering, are neutralized with alkali to produce soaps.



Rancidity

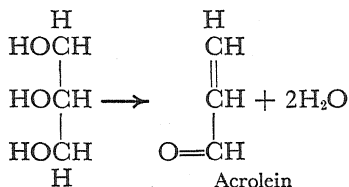
You are all familiar with the objectionable odors and flavors which develop in fats when they become rancid. You are aware,

These reactions may be induced or accelerated by the presence of moisture, air, light, heat, or the hydrolytic enzymes, lipases, which are present in most natural fats. (See "Enzyme" in Chapter 26.) For example, home prepared lard is best stored in a cool dry place, in an opaque container, with only a small area exposed to the air. Also, the rapidity with which mayonnaise becomes rancid is well known.

Antioxidants are organic substances which protect fats from oxidation presumably by being more readily oxidized. Some natural oils contain antioxidants. They are added to many commercial shortenings to delay rancidity. Considerable investigation of antioxidants has been carried on and a large number of quite different organic substances are used in small amounts. Some are acids such as citric and tartaric which have alcoholic groups as well as carboxylic. Others are phenols such as hydroquinone and catechol. Tocopherol and the lecithins have antioxidant action. There are many other substances which are used for one product or another.

Smoke Point

When fats are used for frying or deep fat frying, the smoke point is of some importance. This is the temperature at which the fat begins to smoke. This is always disagreeable for the cook because a smoking fat produces acrolein, by dehydration of glycerol.

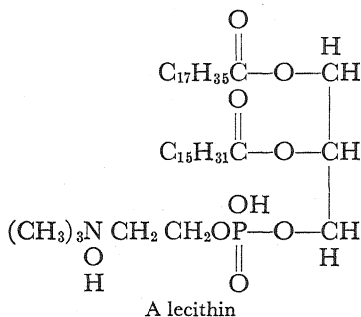
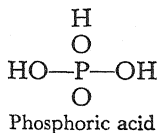
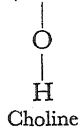
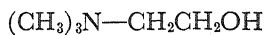


Acrolein is a gas with a sharp odor which irritates the membranes of the eyes and nose. Foods fried in smoking fats frequently have a distinctive and disagreeable flavor.

COMPLEX LIPIDES

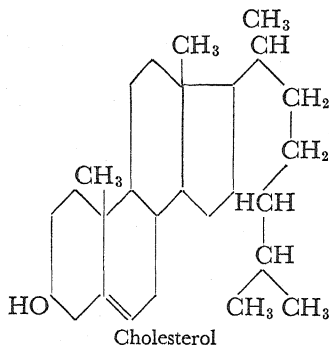
Complex lipides are present in active tissue. They are present in cells where metabolism is relatively rapid while neutral fat is held primarily in the adipose tissues. Blood as well as brain and nervous tissue contains complex lipides.

The phospholipides are closely related to neutral fats, but in their structure one fatty acid is replaced by phosphoric acid joined to an amine. In *lecithins*, the amine is choline, while in the *cephalins* it is amino ethyl alcohol.



STEROLS

The sterols are complex alcohols with a basic ring structure which is common to many substances of great physiological importance, the steroids. The sterols occur widely distributed in the plant and animal kingdom. In man, cholesterol and 7-dehydro cholesterol are present in skin, blood, and bile.



The complete role of these alcohols in the metabolism of man or other species is only partially known. But the close chemical relationship between them and other physiologically active compounds indicates that they may be of great importance as metabolic intermediates. Some steroids which are related to sterols are the following.

Compounds Related to Sterols

1. Male and female sex hormones.
2. Vitamins D (ten have been identified).
3. Bile salts.
4. Adrenal cortical hormones.

NEW TERMS

Lipide, fatty acids.

QUESTIONS

1. On what properties is the classification of organic compounds known as lipides based?
2. What is a fat? How does it differ chemically from other lipides?
3. What is the chemical difference between an oil such as corn oil and a solid fat such as mutton tallow? How may an oil be changed to a fat which is a solid at room temperature?
4. What is saponifaction? Show a typical reaction. What is a soap?
5. What reactions occur when a fat becomes rancid. What factors promote rancidity? What delays it?
6. When a fat smokes, it gives off a gas which stings our eyes and noses. What is this compound?
7. What is a complex lipide? Where do they occur in the body?
8. Give the formula for a phospholipide and point out the difference between it and a true fat.
9. What are the sterols? List some of the compounds which are of utmost importance in the body which are related to the sterols chemically.

Carbohydrates

CHEMISTRY OF THE MAJOR ORGANIC COMPOUNDS OF FOODS

ASYMMETRY AND STEREOISOMERISM

You will remember that early in the study of organic chemistry, the phenomenon of *isomerism* was described. For example, the formula C_2H_6O represents two compounds each with a different arrangement of atoms within the molecule, CH_3CH_2OH and CH_3OCH_3 . Now with the study of carbohydrates it is necessary to describe another type of isomerism, stereo- or space isomerism. Carbohydrates may have the same empirical formula, the same molecular formula, and even the same groups, but if these groups are arranged differently in three-dimensional space, then the compounds will be different in cellular reactions.

Before an attempt is made to explain stereoisomerism in terms of carbohydrates, smaller molecules, simpler compounds will be described to see what a different arrangement in three-dimensional space means. Imagine the carbon atom in three-dimensional space with its four valence forces radiating from a central point like lines or wires in space. If these wires are equally distant from one another it has the shape of a tetrahedron.

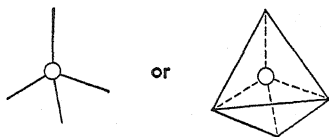
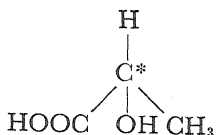
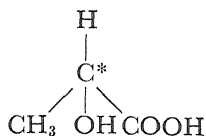


Fig. 24-1. Tetravalent carbon.

Now if each group attached to the carbon atom is different, there will be two possible arrangements in three-dimensional

space, and the two compounds represented by these models will be different. The carbon atom is said to be *asymmetrical*. Get



some models and prove to yourself that there are two and only two arrangements possible. For example, lactic acid has four different groups around the carbon marked with an asterisk. Two lactic acids exist, one present in muscle and the other produced by some bacteria. These two compounds are alike in their chemical properties and in such physical properties as their melting point, solubilities, etc. But they are different in their

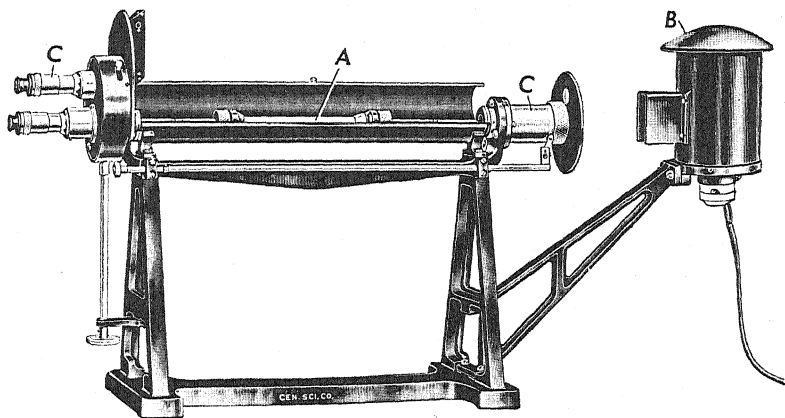


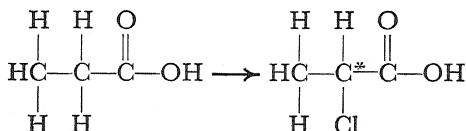
Fig. 24-2. Polarimeter for determining optical activity. A solution of the compound is placed in tube A and the case is closed. The lamp, B, is a source of monochromatic light. C contains polarizing crystals. (Courtesy of Central Scientific Company.)

physiological properties and also in one physical property called *optical activity*. In three-dimensional space, one is the *mirror image* of the other.

Optical activity is the ability of a compound or a solution of a compound to rotate the plane of plane polarized light. A beam of light may be considered to be made up of many waves of light oriented in different planes. When this light is passed through a polarizing prism (for example a quartz crystal) all

the waves are screened out except one with a definite plane. The beam of light emerging from the crystal has waves oriented in only one plane. When this beam of light is passed through a compound or solution of a compound containing an asymmetric carbon atom, the plane of the polarized light is rotated. For example, a solution of muscle lactic acid will rotate the plane of plane polarized light to the right. The amount of rotation will depend upon the concentration of the lactic acid in the solution and the distance through the solution that the light traverses. In a solution of the other lactic acid of equal concentration and equal depth, the light will be rotated an equal amount, but in the *opposite direction*. One form of the lactic acid is called *l*-lactic acid (levo- or left) and the other is called *d*-lactic acid (dextro- or right), depending on which direction the plane of the light is rotated. In a solution of equal amounts of the two forms, the light will not be bent at all. This is called an *inactive* or *racemic mixture* of the two forms.

When an asymmetric carbon atom is obtained through synthetic methods, a racemic mixture is prepared. For example if propionic acid is converted into α -chloropropionic (1-chloropropionic) acid, there is as much chance that the *levo* form will



be prepared as the *dextro*. The resultant product will have equal amounts of each form and will thus be inactive. Asymmetric carbon atoms synthesized by reactions in living cells usually have only one arrangement, one configuration, and are therefore active compounds as far as plane polarized light is concerned.

The number of isomers possible is a function of the number of asymmetric carbon atoms in a molecule. It is equal to 2^n , where n is the number of asymmetric carbons.

If there is one asymmetric carbon atom in a possible arrangement of atoms within the organic molecule, two forms, an *l* and a *d*, are possible. Lactic acid has one asymmetric carbon atom and two forms. When there are two asymmetric carbon atoms, there are four (2^2) possible forms, while with three asymmetric carbon atoms there are eight isomers (2^3).

Significance of Optical Activity

Space isomers differ not only in their optical activity but also in their physiological properties. A physiological property is the effect of a substance on an organism. The effect of adrenalin on blood pressure is one of its physiological properties. In compounds which are used or produced by living cells, the configuration of the molecule is of utmost importance. You can readily prove this to yourself by tasting glucose and galactose, two compounds with like structure but different configuration and quite different to your taste buds in their sweetness. Adrenalin is fifteen times more active in a mammalian organism than its mirror image; while the role of *l*-lysine, one of the essential amino acids, cannot be filled by an infinite amount of the *d*-form.

CARBOHYDRATES DEFINED

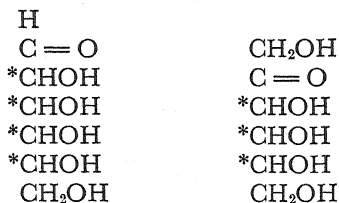
The term "carbohydrate" arose from the observation that a group of organic compounds composed of carbon, hydrogen, and oxygen had a ratio of hydrogen to oxygen of one to two, the same ratio as in water, H_2O . For example, the compound in our sugar bowls, has the molecular formula $C_{12}H_{22}O_{11}$ and from this standpoint alone might be considered a molecule of 12 carbon atoms and 11 water molecules. Actually, these substances are not hydrates at all. They are not readily decomposed by gentle heating into water and carbon but instead form caramel mixtures. They do not have a vapor pressure, and they are not synthesized from the reaction of water on carbon.

A rough definition of carbohydrates would include all crystalline organic compounds which are soluble in water and sweet to taste, and the compounds related to them. *Chemically they are defined as polyhydric (many OH groups) aldehydes or ketones, or their anhydrides.* This classification includes the monosaccharides, the disaccharides, and the polysaccharides, substances all important as far as our food and body chemistry are concerned.

MONOSACCHARIDES

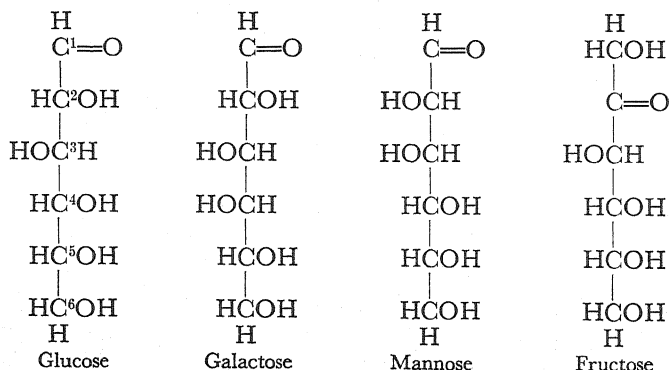
The monosaccharides are carbohydrates (polyhydric aldehydes or ketones) which can not be hydrolyzed. Four monosaccharides occur in our diet or are formed in digestion in our

gastro-intestinal tract. These all have the molecular formula $C_6H_{12}O_6$, and since they have six carbon atoms, are called *hexoses*. Glucose, galactose, and mannose are polyhydric aldehydes, while fructose is a polyhydric ketone. Their formulas are:



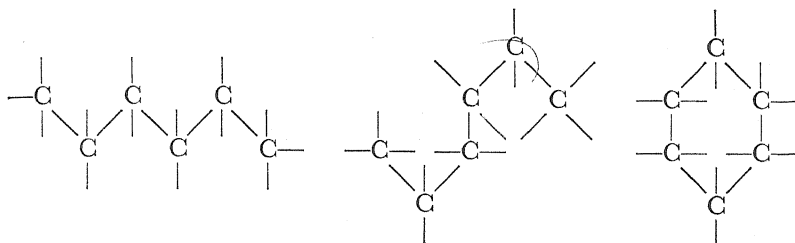
This formula shows the structure of glucose, fructose, galactose, and mannose.

If you look carefully at the formulas, you will see that the carbons marked with asterisks are asymmetric carbons. Thus glucose has four asymmetric carbons while the right-hand formula (fructose) has three. This means that the left-hand formula stands for a possible 16 compounds ($2^4 = 16$) while the right-hand formula stands for a possible 8 compounds ($2^3 = 8$). Glucose, galactose, and mannose are three of the possible forms with the left-hand formula while fructose is the only important one of the possible 8 for the right-hand formula. There is a convention for arranging groups of atoms on two-dimensional paper such as this to represent different three-dimensional arrangements. Thus the projection structural formulas for the compounds are:

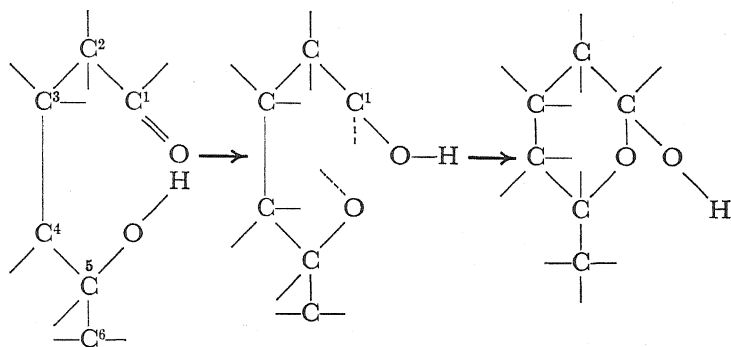


Ring Form

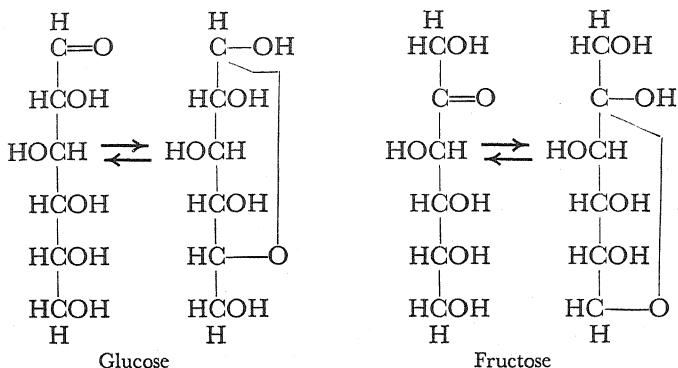
In solutions the monosaccharides exist predominantly in the form of ring compounds in equilibrium with the aldehyde, straight-chain form. In three-dimensional space the straight chain form is not actually *straight* but because of the angles between the carbon-carbon bonds, the molecules are bent around in various shapes. There is free movement at the carbon-carbon bond and one particular molecule may show changes in



its shape from moment to moment. When carbon 1 and carbon 5 are close together, the hydrogen of the —OH group on carbon 5 is close to the oxygen on carbon 1. The hydrogen may migrate to this oxygen and a chemical bond will then be established between carbon 1 and the oxygen on carbon 5 to form a



ring containing five carbons and one oxygen. This ring form is in dynamic equilibrium with the aldehyde — it is constantly forming the aldehyde while the aldehyde is constantly forming the ring compound.



(In the above formulas the ring form is written in a straight line with long bonds between the oxygen and carbon to emphasize its close relationship to the straight-chain compound. In reality, these bonds are no longer than ordinary bonds.)

H
|

The —COH, which includes carbon 1 in the ring form, is called a *potential aldehyde* since it can quickly rearrange to produce an aldehyde. If a reaction reduces the concentration of the aldehyde, the ring form will rapidly produce more. Likewise the —COH group on carbon 2 of fructose is called a *potential ketone* since it can rapidly rearrange to form the ketone group.

Occurrence of Monosaccharides

Of all the possible monosaccharides, only glucose and fructose occur free in significant quantities.

Glucose (dextrose, grape sugar) is widely distributed in plant and animal materials. It is present in fruits, vegetables, flowers, sap, blood and diabetic urine and in very small amounts in normal urine. It is produced during digestion of starches, glycogen, sucrose, lactose, and maltose.

The term "glucose" was formerly widely applied to the syrup now more commonly called corn syrup. This mixture does contain the monosaccharide glucose, but other carbohydrates, some

inorganic substances, and water, are also present. The syrup is produced by hydrolyzing cornstarch (occasionally other starches) with HCl or H_2SO_4 until a starch iodide test is no longer obtainable. The mixture is then neutralized with Na_2CO_3 , decolorized, and concentrated. The carbohydrates contained in the final product are dextrans, maltose, and glucose.

Beside the wide use of glucose as a food, it is used as a reducing agent in the silvering of mirrors, in the production of rayon, and for the production of a wide number of fermentation products (ethyl alcohol, citric acid, etc.).

Galactose does not occur free but as part of the molecule of a disaccharide, a polysaccharide, or a complex lipid. When these substances are hydrolyzed, galactose is produced. Lactose, the sugar of milk, is a disaccharide which yields on hydrolysis, galactose and glucose. A group of polysaccharides called galactans are anhydrides of galactose and occur in agar, gums, and fruit pectins. The cerebrosides, a group of complex lipides, yield galactose on hydrolysis.

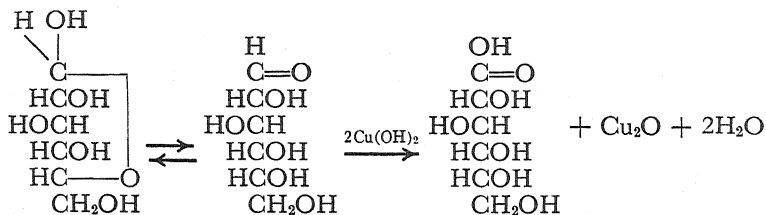
Mannose occurs in small amounts in some protein molecules such as serum albumin and globulin.

Fructose occurs in vegetables, fruits, flowers. It frequently is accompanied by glucose and sucrose. Hydrolysis of sucrose yields fructose and glucose. The polysaccharide, inulin, which occurs in Jerusalem artichokes, is an anhydride of fructose. Fructose syrup has been produced from this polysaccharide by hydrolysis with dilute HCl . Since fructose is the sweetest tasting of the monosaccharides, it makes a very acceptable syrup.

Chemical Reactions

Oxidation Most of the tests for the detection of monosaccharides depend on oxidation reactions. For example, to detect glucose in urine, a few drops of urine are added to a solution containing cupric ion and having, therefore, a blue color. The mixture is warmed. If the urine contains glucose, or any other monosaccharide, a precipitate of cuprous oxide, Cu_2O , is formed. This may vary in color from bright yellow, through red to brown, depending on the size of the particles formed. In this reaction, the aldehyde group of the glucose is readily oxidized to

a carboxy group, while the Cu^{++} is reduced to Cu^+ . This may be represented schematically as follows:



The acid (gluconic acid) formed may be further oxidized.

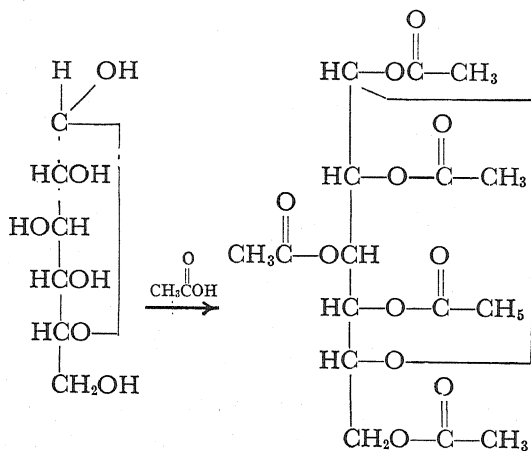
Many solutions are used to detect carbohydrates, but all are alkaline solutions of the oxides of copper, mercury, bismuth, or silver. Changes in concentration and $p\text{H}$ alter the sensitivity of the tests and the stability of the solutions. A few of the cupric solutions have the following composition:

Fehling's CuSO_4 , KOH and sodium potassium tartrate.

Benedict's CuSO_4 , Na_2CO_3 and sodium citrate.

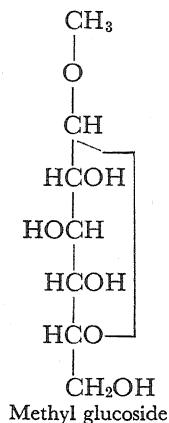
Barfoed's $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ and CH_3COOH .

Acetylation Since monosaccharides contain hydroxyl groups, they react similarly to other alcohols in forming esters. For example, acetates may be prepared according to the following equation:



One or more OH group may be acetylated. This type of reaction is important in the formation of Acetate rayon, where some of the hydroxyl groups in cellulose are acetylated.

Glucosides As alcohols, the monosaccharides also have the ability to form ethers. According to the ring formula for glucose, it has six hydroxyl groups. All these may form ethers, although the most reactive is the OH formed when the ring closes (1- or top OH). When glucose reacts with methyl alcohol in the presence of HCl, methyl glucoside is formed.



The term "glucoside" is a rather loose one, used for any compound which yields glucose on hydrolysis. A "glycoside" is a substance which yields a monosaccharide on hydrolysis.

DISACCHARIDES

Disaccharides are organic substances which on simple hydrolysis yield two molecules of monosaccharides for each molecule of disaccharide. Those which are of importance in the diet and body chemistry are sucrose, maltose, and lactose.

Sucrose is the sugar which occurs in sugar cane and sugar beets and which, after extraction and purification, appears in our sugar bowls. It is also present in a large number of other fruits and vegetables, frequently accompanied by glucose and fructose. The American people consume large quantities of this almost pure carbohydrate.

Sugar per Capita Disappearance in U. S.
Calculated as Pounds Refined

<i>Year</i>	<i>Pounds</i>
1939	100.4
1940	108.0
1941	92.4
1942	82.9
1943	93.6
1944	100.2
1945	71.2
1946	82.9

(The consumption of a food which contains nothing but carbohydrate frequently accounts for the occurrence of poor diets in



Fig. 24-3. Beet sugar field. (Courtesy of United States Beet Sugar Association.)

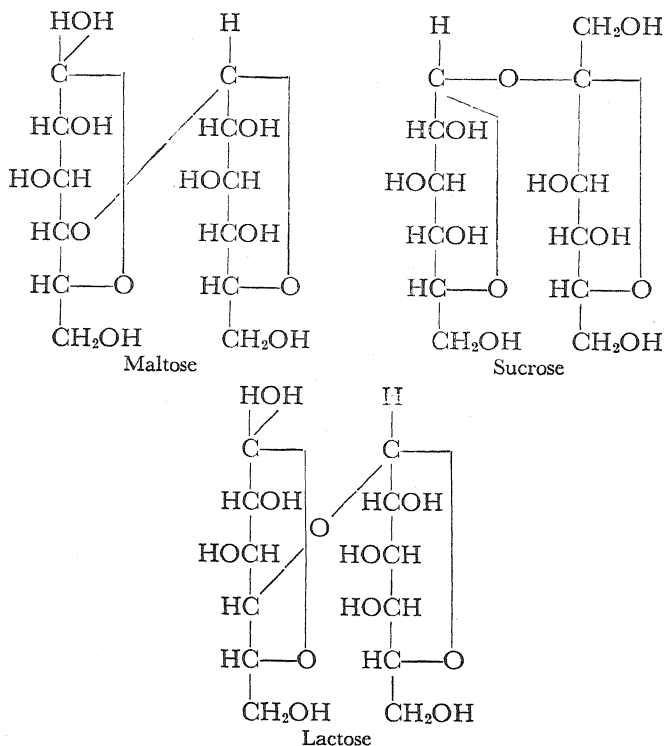
people who have the means of procuring an excellent one.) On hydrolysis sucrose yields glucose and fructose.

Maltose does not occur very widely distributed in nature, but is produced during digestion. It is present in sprouting grains and whenever starch is partially hydrolyzed. It is present in corn syrup to the extent of 26 per cent and is said to be produced in the brown crust of bread. On hydrolysis it yields two molecules of glucose.

Lactose is present in the milk of all mammals and is the only carbohydrate present in milk. It is interesting that although the carbohydrate is always the same, the average quantity may vary considerably with species. For example, human milk contains 6.9 per cent while reindeer is as low as 2.5 per cent [Wright, Deysher, and Cary, U. S. Department Agriculture, Yearbook, Separate No. 1704 (1940)]. Lactose yields on hydrolysis, glucose, and galactose.

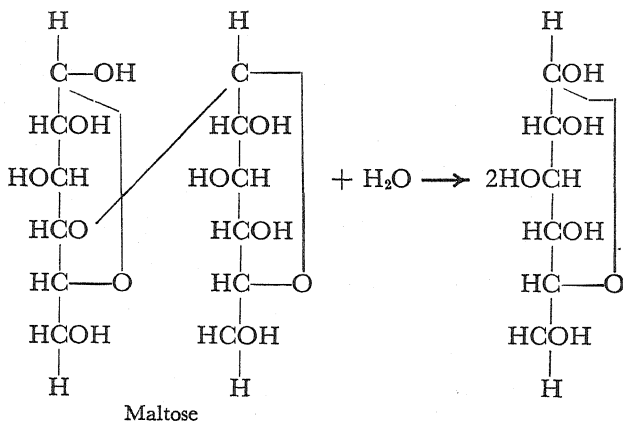
Structure of the Disaccharides

The structural formulas for the disaccharides are the following:



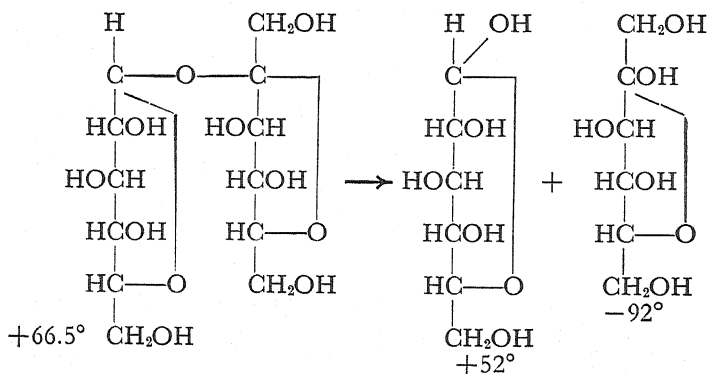
The monosaccharides are joined by a glycoside link. You will notice that both maltose and lactose have a potential aldehyde group and that they are, therefore, reducing sugars. Maltose is

a glucose glucoside and on hydrolysis it forms two molecules of glucose. Lactose is glucose galactoside and yields one molecule of glucose and one of galactose on hydrolysis.



In sucrose, on the other hand, both the potential aldehyde and potential ketone groups are involved in the glucoside (or fructoside) link and it is, therefore, not a reducing sugar. However, when sucrose is hydrolyzed, glucose and fructose are produced. They are reducing sugars.

Invert sugar is the name given to the equimolecular (one molecule for one molecule) mixture of glucose and fructose which is produced on hydrolysis of sucrose. The mixture bears this name because the plane of polarized light is reversed when sucrose is hydrolyzed.



Sucrose is dextro-rotatory, while in the mixture fructose is more strongly levo-rotatory than glucose. The result is a rotation to the left.

POLYSACCHARIDES

All the polysaccharides which are most important in foods are polymers of glucose. They are made up of strings of glucose residues joined together in the same fashion that two glucose residues are joined in maltose. (The configuration of the

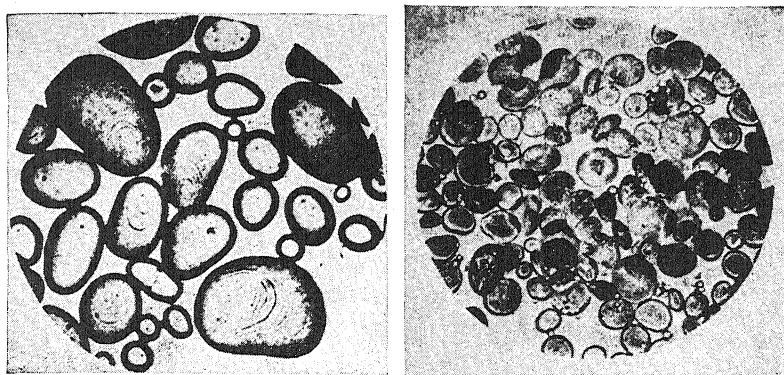


Fig. 24-4. The left photomicrograph is of starch granules from potatoes while the right is of starch granules from wheat. (Courtesy of Reichert, The Differentiation and Specificity of Starches, Carnegie Institution of Washington.)

1-carbon, the potential aldehyde, is not the same in all.) They are the starches, the dextrins, the hemicelluloses, celluloses, and glycogen. All are insoluble in water.

Starches are present in many fruits and vegetables. The starch granule is characteristic of the plant from which it is obtained. Thus, potato and wheat starch may be differentiated by the appearance of the starch granules under the microscope.

In cold water, starches show little tendency to swell. But as the temperature of the water is raised, there is an increased tendency for the granules to swell. At length a temperature is reached at which the number of granules swelling increases markedly and many granules burst. This is known as the *gelation temperature* or thickening point and varies with the source of the starches [Cornstarches have a range from 64–71°. Dox

and Roark, *J. Am. Chem. Soc.*, **39**, 742-745 (1917)]. Hydration of the polysaccharide molecules appears to occur under these conditions. For discussion of gelation see Gortner, *Outline of Biochemistry*, Second Edition, p. 668, or Lowe, *Experimental Cookery*, Third Edition.

The starches produce a characteristic blue color in the presence of iodine. This is a reaction which gives a noticeable color in the presence of very low concentrations of either starch or iodine. It is frequently used as a test for starches.

The *dextrins* are produced when starches are hydrolyzed with acid or enzymes. These substances give colors in the presence of iodine, from purple through red to colorless, depending on the size of the molecule, and are named according to the color produced — erythrodextrin (red), achroodextrin (colorless). As the hydrolysis proceeds the molecule is probably shortened two glucose residues at a time and maltose is the side product. Dextrins are therefore produced in small amounts during cooking of starches and during digestion.

Glycogen is the polysaccharide which occurs in the tissues of animals. It is present in fair amounts in liver and in smaller amounts in muscle. On hydrolysis it yields only glucose and appears to contain some twelve or fourteen of these residues per molecule.

Hemicellulose and *cellulose* are large molecules which make part of the structural units of plants. Strings and fibers in plants are frequently predominantly cellulose. Chemically cellulose is made up of 100 to 200 glucose residues while hemicellulose may contain fewer.

Celery, cabbage, and spinach all have cellulose. Cotton, hemp, linen, and wood also contain cellulose as structural units. Cellophane is almost pure cellulose which is made by a process similar to that used for the production of rayon. Rayon, too, is composed of cellulose.

PROPERTIES

Since all of the polysaccharides are made up of large molecules, they form colloidal dispersions in water. The exact size and composition of the molecules is still receiving study to try and answer the question completely. Starches are probably mole-

cules which are composed of 24 to 30 glucose residues cross linked to form macro molecules composed of multiples of these units. It has been estimated that there are 1500 glucose units in a starch molecule. This would mean that approximately 50 of the "linear units" each with 24 to 30 glucose residues are cross linked to make up the molecule. There is fairly good agreement that the length of the "linear unit" in cornstarch and in potato starch are different. Whether starches contain one, two or more different molecules is still hotly debated by workers in the field. All starches contain residues which are not carbohydrate in nature, such as phosphate, silicate, fatty acids and other lipides, calcium, magnesium, sodium, and potassium ions.

The question of the structure of glycogen is in a similar state of flux. The "linear unit" in glycogen is believed to be smaller, with only 12 to 15 glucose residues.

Cellulose appears to be a larger molecule than either of these groups of polysaccharides.

On hydrolysis with acid all of the above polysaccharides produce glucose. On enzymatic hydrolysis with diastase or with digestive enzymes, starches and glycogen form maltose while cellulose is not affected. Some microorganisms produce enzymes capable of hydrolyzing cellulose. In the decay of wood, this reaction occurs.

The polysaccharides do not reduce Fehling's solution or any of the copper reducing solutions. This is probably the result of a small number of potential aldehyde groups compared to the size of the molecule. Or it may be that the potential aldehyde groups are covered up by other parts of the molecule.

AVAILABLE CARBOHYDRATE

The term "available carbohydrate" is used to classify fruits and vegetables in dietetics. There are several methods for classifying these foods: 1, 3, 5, 7% or 5, 10, 15, 20% fruits and vegetables. It is a useful and convenient classification when calculating diets, since an average serving of a 5% vegetable will give approximately the same number of calories as an average serving of another 5% vegetable. "Available carbohydrate" represents the carbohydrate which is capable of direct absorption or digestion and absorption by human beings. Molecules such as

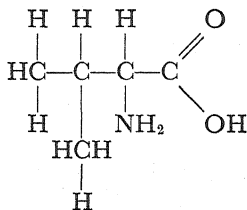
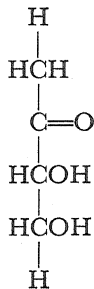
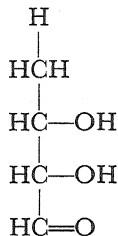
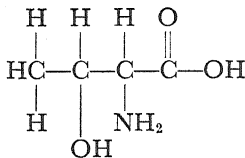
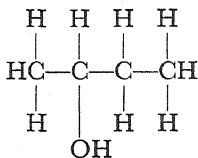
cellulose, pentosans, lignins which escape digestion would not be included in the estimation. It has been observed that some cellulose disappears during passage through the gastro-intestinal tract, the amount varying with individuals and the amount consumed. This may amount to as much as 50 per cent of the cellulose ingested. Since no digestive enzyme capable of effecting the hydrolysis of cellulose has ever been demonstrated, it is suspected that the cellulose disappears in the colon through bacterial action.

NEW TERMS

Stereo- or space isomerism, asymmetric carbon atom, optical activity, racemic mixture, carbohydrate, monosaccharide, disaccharide, polysaccharide, available carbohydrate.

QUESTIONS

1. Why is optical activity important in our bodies? What compounds show optical activity?
2. What is the difference between an asymmetric carbon atom and one which is symmetrical? What is the difference between space isomers?
3. Pick out the asymmetric carbons in each compound and mark them with asterisks. How many space isomers will exist for each formula?



4. What is a monosaccharide? How does it differ from a disaccharide? Give examples of each.
5. Show the ring structure for glucose. What is a potential aldehyde group? Circle the potential aldehyde group in glucose.
6. Give the equation for the oxidation of glucose by a reducing agent such as Benedict's solution. Will fructose reduce Benedict's solution? Why?
7. List the sources of glucose in your diet.
8. How do you account for the fact that the per capita consumption of sugar is very high? Why is this alarming?
9. Will sucrose reduce Fehling's solution? Why? Maltose?
10. What is invert sugar? How is it formed?
11. What is the difference in chemical structure between starches and glycogens?
12. What is the meaning of "available carbohydrate"? What carbohydrates are included under this category?

Proteins

CHEMISTRY OF THE MAJOR ORGANIC COMPOUNDS OF FOODS

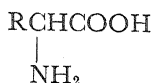
The protoplasm and the nucleus of all cells contain a group of organic compounds which are called proteins. These molecules appear to be essential to the life of the cell since no cells are known to exist without protein and since a chemical change in the protein frequently quickly kills the cell. Protein molecules contain carbon, hydrogen, oxygen, nitrogen, and sulfur, and some proteins contain other elements as well, such as phosphorus, iron, or cobalt. The molecular weight of these proteins is very high ranging from 15,000 for the light-weight protein, insulin, up to 60,000,000 for influenza virus.

The number of different proteins which exist in nature is thought to be very great. Unlike the carbohydrates where there is only one glucose and one lactose, there are many different proteins in one animal body, and they are usually different from those occurring in another species. For example, in your own blood stream, there are an albumin and a globulin fraction and in this globulin fraction there appears to be a large number of proteins: some of those important in blood clotting, those developed in immunity, those concerned with blood groups, and a series of lipoproteins.

The blood albumin from one species appears to be different from that of another species. For example, if the albumin fraction is isolated from the blood of a dog and injected into a rabbit it acts as a *foreign protein*. The rabbit becomes sensitized and on further injection suffers allergic shock and perhaps dies. The sensitivity which man builds up to horse serum, depends on the fact that although proteins in horse serum are similar to those in

human blood, they are not identical. There are an enormous number of different proteins in nature, each characteristic not only of the place where it is found, such as blood, but also characteristic of the species. This is called *protein specificity*.

On hydrolysis proteins yield a mixture of some 20 to 22 amino acids, substances which with two exceptions have the general formula:



These are called alpha-amino acids since the amino group, NH_2 , is attached to the first, or alpha, carbon adjacent to the carboxyl group.

In 1908 the American Physiological Society and the American Society of Biological Chemists adopted a classification of pro-

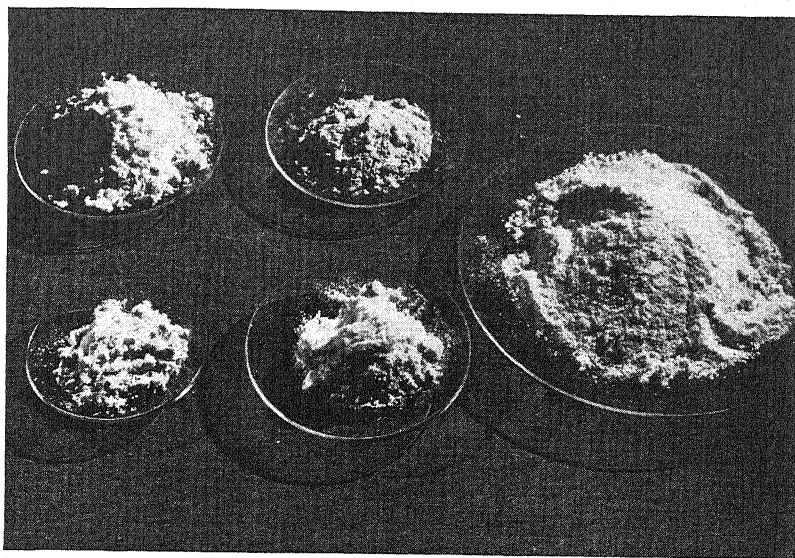


Fig. 25-1. Five protein fractions from a pint of human blood. These are not necessarily pure proteins but are groups of proteins with similar physical properties. The fractions from left to right are: (back) globulins including thrombin necessary for blood clotting and the proteins for blood grouping, other globulins, (front) fibrinogen which reacts with thrombin to produce a blood clot, immune globulin which contains the proteins which confer immunity to some diseases, and albumin. (By LIFE photographer Fritz Goro. Copyright TIME Inc.)

tein based on the solubilities (colloidal dispersibility) of proteins and what was then known of their chemical structure. The names assigned to the various groups are in wide use, and it is worth while for you to be able to recognize those terms.

Simple proteins yield only amino acids on hydrolysis. Actually careful studies of some of the proteins included in this classification have shown that they contain small amounts of carbohydrates. Where the classification says "soluble," it means that the protein is readily dispersed colloiddally. The protein molecule is too large to form a true solution. The complete solubility data will not be given and only a few of many possible examples indicated.

1. Albumins are soluble in water and precipitated by heat. Examples: egg albumin, lactalbumin from milk, legumelin from peas.

2. Globulins are insoluble in water, soluble in dilute neutral salt solutions, and precipitated by heat. Examples: serum globulin of blood, edestin in wheat and hemp seed, tuberin in potato.

3. Glutelins are insoluble in water, but soluble in dilute acid or alkali, and do not precipitate with heat. Examples: glutenin of wheat and oryzonin of rice. There are no known animal proteins of this type.

4. Gliadins or prolamins are insoluble in water, but soluble in 70 to 90% alcohol and are not precipitated with heat. Examples: gliadin of wheat, zein of corn, hordein of barley. These are proteins which have been found only in cereals.

5. Albuminoids are insoluble. Examples: keratin of hair, horns, and nails, collagen of bone and cartilage, fibroin of silk.

6. Histones are soluble in water and precipitated by heat. They are slightly basic in reaction. Examples: globin of hemoglobin, thymus histone, and proteins from spermatozoa.

7. Protamines are soluble in water and not precipitated by heat. They are strongly basic in reaction. Examples: proteins from spermatozoa of fish.

Conjugated proteins yield on hydrolysis some other molecule besides the amino acids. This is called the prosthetic group.

1. Phosphoproteins yield phosphoric acid as well as amino acids. Examples: casein of milk, vitellin of egg yolk.

2. Nucleoproteins yield amino acids plus nucleic acids, complex organic molecules. They are believed to be present in the nuclei of all cells.

3. Lecithoproteins yield lecithin and amino acids.

4. Chromoproteins contain amino acids and a color-bearing prosthetic group. Examples: the hemoglobins, cytochromes widely distributed in many forms of life, Mollusca, Chordata, Arthropoda, etc.

5. Glycoproteins contain a carbohydrate residue along with the amino acids. Examples: mucins, mucoid of tendons.

The derived proteins are an indefinite group including all high molecular weight molecules which are produced when proteins are partially hydrolyzed.

1. Metaproteins are very large molecules similar to the original protein. They are soluble in dilute acid or dilute alkali. They are, of course, colloidal.

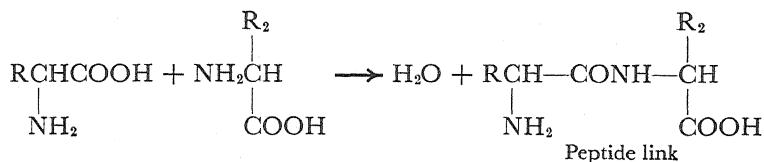
2. Proteoses form colloidal dispersions in water, but are not precipitated by heat.

3. Peptones form true solutions.

4. Polypeptides are much smaller molecules than the original protein and form solutions in water.

CHEMICAL STRUCTURE

The chief method by which the amino acids are held together in proteins is the peptide link. If the carboxyl group of one amino acid reacts with the amino group of another, a peptide link, —CONH— , is formed and the product is called a dipetide.



On hydrolysis the reaction is reversed. When a large number of these peptide links are formed, a polypeptide is produced. But a protein molecule is more than a polypeptide string. The complete structure of the protein molecule is not known as yet, but it is known that within the molecule there are bonds which hold parts of the polypeptide string together and that the amino

acids in these strings tend to be arranged according to certain patterns. The shape of protein molecules can be detected by several devices, among them the electron microscope. Some proteins such as silk fibroin, and hair albuminoid appear to be long, thin cylinders, others are globular, and still others are

RELATIVE DIMENSIONS OF VARIOUS PROTEINS

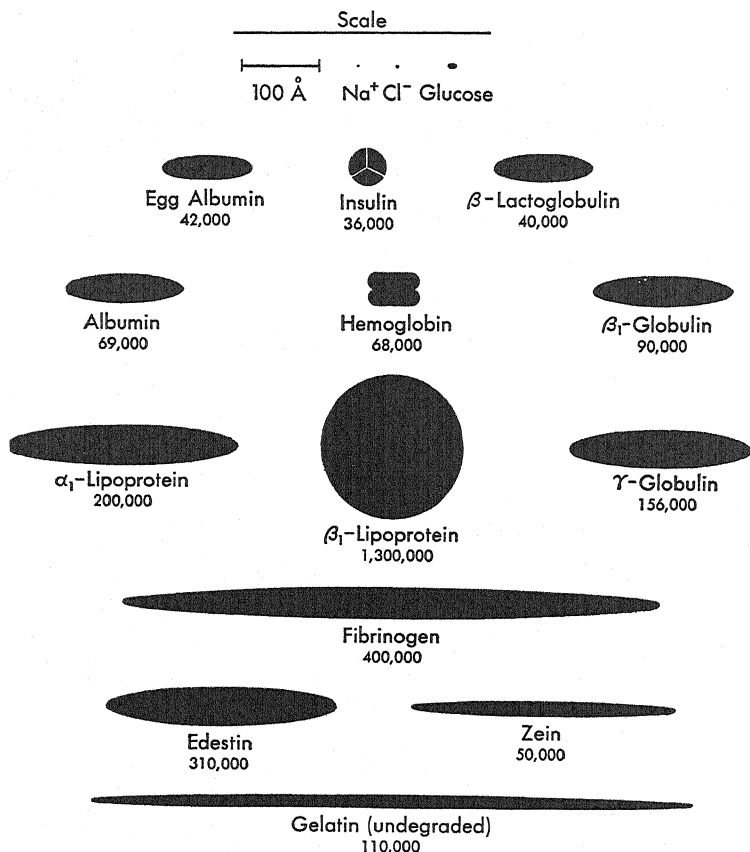


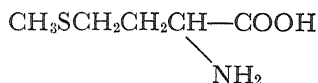
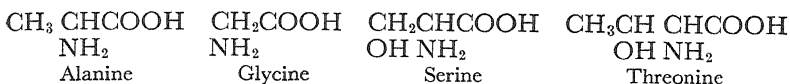
Fig. 25-2. The numbers under the models of the protein molecules are their approximate molecular weights. (Courtesy of Dr. J. L. Oncley)

shaped like tiny footballs. The whole problem of protein structure cannot be dealt with here. Adequate discussion of this interesting subject may be found in recent texts on biochemistry and in the Annual Review of Biochemistry.

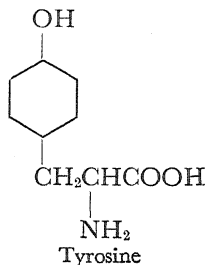
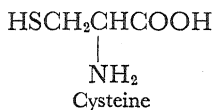
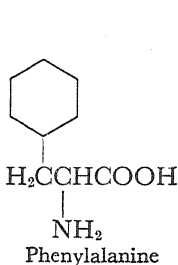
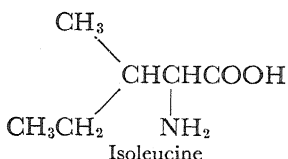
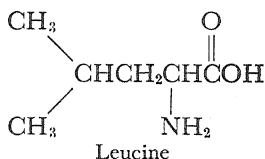
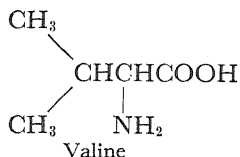
At the beginning of the chapter, it was mentioned that proteins are made up of about twenty-two different amino acids. These are organic molecules with a great difference in structure. All except two are alpha amino acids and these two (proline and hydroxy proline) are closely related. It is interesting that the configuration (arrangement in space) of the groups about the alpha carbon is always the same in all the amino acids. If an amino acid with the opposite configuration is synthesized chemically, it cannot be used to build protein by a living cell, unless the configuration can be changed to that which is typical.

Common Amino Acids

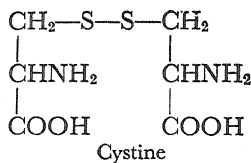
Monoamino, monocarboxylic



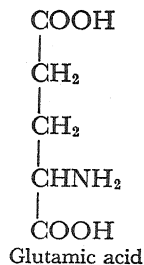
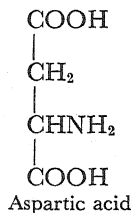
Methionine



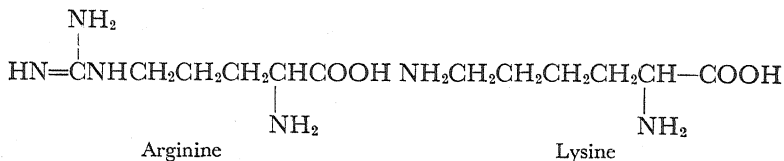
Diamino, dicarboxylic



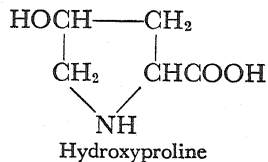
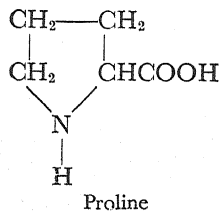
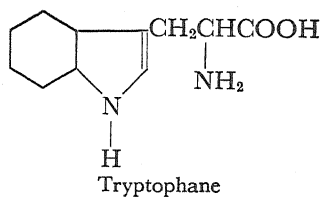
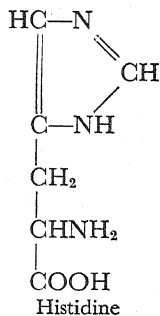
Monoamino, dicarboxylic



Diamino, monocarboxylic



With heterocyclic rings

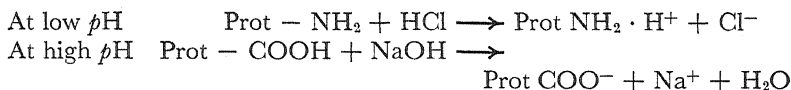


Amino Acid Content of Edible Portion of Meat in Per Cent of the Protein
($N \times 6.25$) *

	Whole Egg (Block)	Whole Milk	Beef	Pork	Lamb	Veal
Arginine	6.4	3.5	6.4	6.4	6.2	
Histidine	2.1	2.4	3.9	3.8	3.2	3.5
Lysine	7.2	8.1	8.9	8.7	8.8	
Leucine	9.2	11.8	7.6	7.2	8.1	7.6
Isoleucine	8.0	6.5	5.7	5.7	5.4	5.6
Valine	7.3	6.2	5.3	5.5	5.4	5.3
Methionine	4.1	2.2	2.5	2.4	2.4	
Cystine	2.4		1.4			
Threonine	4.9	4.8	4.5	4.5	4.8	3.9
Tryptophane	1.5	1.4	1.4	1.4	1.4	1.1
Phenylalanine	6.3	4.6	4.2	4.2	4.3	3.8
Glutamic acid			14.2	11.8	11.9	
Tyrosine	4.5	5.5	3.4			
Glycine	2.2		5.0			
Alanine			4.0			
Serine			5.4			
Aspartic acid			6.0			
Proline			6.0			

PROPERTIES OF PROTEINS

Since proteins contain a small number of free carboxyl groups which are acid and a number of free amino groups which are basic, they are amphoteric molecules and with change in pH , change their reaction:

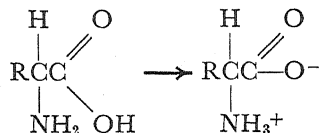


Thus at a low pH the protein exists as a positive ion, while at high pH it is a negative ion. At some intermediate pH this ionization is a minimum and a *zwitter ion* is formed. This intermediate pH is called the *isoelectric point* of the protein and can be defined as the pH at which ionization of the protein to form either

* From M. Sahyun, *Proteins and Amino Acids in Nutrition*, p. 204. Copyright, 1948, by Reinhold Publishing Corporation and used with their permission.

a positive or a negative ion is at a minimum. The isoelectric point of a protein need not be 7 since the number of amino groups and carboxyl groups is not equal.

The *zwitter ion* is a neutral ion possessing a positive and negative charge. Here it is formed from the interaction of the amino group and carboxyl group. Thus the zwitter ion for an amino acid would have the following structure:



It has been pointed out before that the so-called solubility of proteins really refers to their dispersibility. The molecules are so large that they do not form true solutions, but since many are hydrophilic, they are self-peptizing in water. (See Colloidol Dispersions, p. 209.)

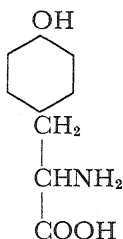
Proteins are precipitated by a number of agents and agencies. Some of these agents have a physical effect on the colloidal dispersion of the protein in water and cause it to precipitate. Others bring about chemical changes in the protein molecule so that it is no longer dispersible in water. The terms "coagulation" and "denaturation" have been applied to both these phenomena. There has been an attempt to use the term "coagulation" to indicate precipitation of the colloidal particles without chemical change and the term "denaturation" for the phenomenon which results from chemical reactions. At present the terms are not precisely used and are frequently confused.

The agents which precipitate the protein, probably with no change in the molecule, are the salt solutions. You will recall that electrolytes precipitate colloidal dispersions, although hydrophilic systems such as proteins dispersed in water are not as sensitive to the effect as hydrophobic dispersions.

Denaturation occurs through the effects of heat, alcohol, alkaloid reagents, such as tannic acid, heavy metal salts, radiant energy, and agitation. You are all familiar with the change which occurs in the albumin of eggs through heating. Some of you have also had the experience of whipping egg albumin until it becomes dry and dull white. The dry dull white precipi-

tate which no longer produces an air foam is the denatured protein. Mercuric chloride is an example of a heavy metal salt which has marked bactericidal powers because it causes denaturation of the protein in the bacteria and hence their death. Alcohol and light have similar effects. Denatured proteins which have been carefully studied appear to be slightly different structurally from the native protein which has produced them. Some have a different number of free carboxyl groups or a different number of free —SH groups.

Proteins are identified by their colloidal behavior and by certain color reactions. The *Biuret test* is a test with dilute CuSO_4 in the presence of NaOH . Proteins and most other compounds containing a peptide link give a violet color. *Millon's reagent* causes protein to precipitate and a red color to develop. This test depends on the presence in the protein of a phenolic hydroxyl. The amino acid tyrosine



has this group, and proteins which contain tyrosine will give a positive Millon's. This amino acid is widely distributed in proteins and the Millon's test is, therefore, a fairly good indication of the presence of protein. Gelatin is an example of a protein deficient in tyrosine and hence negative to Millon's reagent. *Xanthoproteic* (meaning literally "yellow protein") test is a reaction of nitric acid with proteins to give a yellow color which turns deeper in a basic solution. The reaction is a nitration of the benzene nucleus, and the color depends upon the presence in proteins of the amino acids, tyrosine, phenylalanine, and tryptophane which contain this benzene nucleus.

Hopkins-Cole reagent contains glyoxalic acid, CHOCOOH , which in the presence of sulfuric acid gives a purple color with tryptophane. The test is carried out by pouring a layer of the reagent on top of the protein solutions. Proteins which contain

tryptophane (and most do) give the purple color at the junction of the two liquids.

NEW TERMS

Protein specificity, simple proteins, conjugated proteins, derived proteins, isoelectric point, zwitter ion, denaturation, prosthetic group.

QUESTIONS

1. Discuss the structure of a typical protein. How do you account for the fact that our knowledge of proteins is incomplete?
2. What is the peptide link? Show how amino acids are held together in a protein?
3. Give an example of protein specificity.
4. Account for the fact that proteins are amphoteric.
5. How can you account for the fact that the isoelectric point of all proteins is not $pH\ 7$?
6. What is a zwitter ion? Show by chemical formula. Would you expect zwitter ion formation in a protein?
7. Why is a positive Biuret only indicative of a protein, not proof?
8. How may the color tests for proteins be used to *prove* the presence of protein?
9. What is the prosthetic group on conjugated proteins, such as the phosphoproteins? The nucleoproteins? Lipoproteins?

maltose. Introduction of a few milliliters of saliva will cause the hydrolysis of starch and the production of maltose in a few minutes.

SALIVARY DIGESTION

Saliva is a fluid secreted from the three main pairs of glands in the mouth: the parotid in the cheeks, the submaxillary, and the sublingual opening below the tongue, and from the many small buccal glands and the mucous membranes of the mouth, throat, and esophagus. The ropiness of saliva is caused principally by the presence of mucin, a glycoprotein. The composition of saliva varies in different individuals and in the same individual during the day. An average of a number of different samples gave the following composition:

H ₂ O	99.4%
Salts	0.19 (Na ⁺ , K ⁺ , Ca ⁺⁺ , Mg ⁺⁺ , Cl ⁻ , HCO ₃ ⁻ , SO ₄ ⁻⁻ , PO ₄ ⁻⁻⁻)
Organic	0.39 (Mucin, enzyme ptyalin, cell debris)

The pH likewise shows variation but averages pH 6.35–6.85, slightly on the acid side.

The secretion of saliva is stimulated by the presence of foreign material in the mouth and by chemical and psychological means. You are all familiar with the increased flow of saliva when the dentist works on your teeth or when you chew a piece of paraffin. You are also familiar with the “mouth watering” effect of the thought of appetizing food.

The enzyme, ptyalin, is an amylase and when the saliva containing this enzyme comes in contact with food, starches and dextrins begin to hydrolyze. The reaction is probably one by which a molecule of maltose is split from the starch chain each time. The amount of hydrolysis which occurs in the mouth is small, even in individuals who chew their food thoroughly. But in the stomach, before the food comes in contact with gastric juice, there is usually time for considerable salivary digestion. Beazell has shown that 40 per cent of the starch of an ordinary meal remaining in the stomach $\frac{1}{2}$ to 1 hour is digested to maltose. A maltase is also present in the saliva in small amounts and catalyzes the hydrolysis of maltose to glucose.

GASTRIC DIGESTION

When food is swallowed it passes down the esophagus, propelled by wavelike motions called peristalsis, passes through the cardiac sphincter, and enters the stomach. Many of the cells which line the stomach pour out the secretion called gastric juice. There is movement of the stomach wall in the middle portion and the pylorus, which results in some mixing of the food in that region. The fundus is quiet, and food lodged there and in the body of the stomach undergoes salivary digestion without gastric juice admixing. When the food does come in contact with gastric juice the lowered pH prevents further salivary digestion.

Gastric juice contains an average of 0.4 per cent HCl and has a pH of 0.9 to 1. Small amounts of inorganic salts are present, as well as the enzymes pepsin (a protease), a lipase, and mucin, a glycoprotein. The pepsin is not secreted as an active enzyme, but rather as its precursor, pepsinogen. Pepsinogen is then changed into active pepsin through the action of HCl or of some already formed pepsin. Both pepsin and pepsinogen have been crystallized and are found to be proteins. The exact reaction involved in the transformation of pepsinogen to pepsin is not known.

Pepsin catalyzes the hydrolysis of many protein molecules to smaller molecules. Proteoses and some peptones may be produced in the stomach. It also changes the casein of milk to paracasein which then combines with a calcium ion and precipitates as a soft curd. This



Fig. 26-4. X-ray of the stomach after barium sulfate. A small amount has passed into the duodenum and can be faintly seen. (Courtesy of Jackson, Hildreth, Volderauer & Pearson, Radiologists.)

curd is readily hydrolyzed by pepsin. Lipase of the gastric juice is like other enzymes — only effective when there is a surface contact with the substrate. This enzyme is effective with any fat which is emulsified so that it may come in contact with a relatively large quantity. Fats in cream, mayonnaise, egg yolk, etc., are partially hydrolyzed.

As digestion proceeds, the movements of the pylorus become more frequent and more vigorous, and the pyloric sphincter begins to relax intermittently. The mixture of food and gastric juice moves along the stomach wall and is propelled into the duodenum. Protein digestion is by no means complete at this stage. Meat fibers are frequently mascerated and the whole food mass is considerably diluted by the gastric juice (the daily output of gastric juice is approximately 2.5 liters). The mixture of gastric juice, saliva, and food ejected into the duodenum is called chyme.

The HCl of the gastric juice has other functions than that of supplying a desirable pH for peptic digestion of protein. Secondly, it is an important bactericide. A host of bacteria, pathogenic and nonpathogenic, enter the gastro-intestinal tract every day. The importance of an adequate supply of HCl is demonstrated by the increased fermentation which occurs in the stomach when HCl secretion is diminished. Thirdly, HCl may also be important as far as absorption of iron and calcium ions in the upper part of the duodenum. There is some evidence that absorption of these ions is diminished when the gastric chyme does not have a low pH . Fourthly, HCl changes pepsinogen to pepsin.

INTESTINAL DIGESTION

The acid chyme is mixed with the three fluids of the intestine by the vigorous peristaltic motion of the small intestine. In a human being, the opening of the common bile and pancreatic duct (duct of Henley) is a short distance below the pyloric sphincter. Bile and pancreatic juice are mixed with the chyme as it passes this place, and the narrowness of the tube and vigorous motion affect rapid mixing with the intestinal juice produced by cells in the intestinal mucosa (the lining of the intestine). The HCl is neutralized by the bicarbonates present in the pancreatic and intestinal juice, and the food residues begin to be further

digested by the many enzymes present in these fluids. Bile contains no enzymes but it is important in normal intestinal digestion.

Human pancreatic juice has a *pH* of about 8 and contains a large number of enzymes. In the table below these enzymes and their hydrolytic activities are given. The intestinal juice probably contains only enterokinase and amylase (Wilhelmi, Chapter X, p. 342) but the cells which line the intestine contain enzymes which are effective in digestion. All these enzymes are listed together.

<i>Pancreatic</i>	<i>Intestinal Juice and Intracellular Digestive Enzymes</i>	<i>Activity</i>
Amylase (amylpsin)	Amylase	Starch \longrightarrow maltose
Maltase	Maltase	Maltose \longrightarrow 2 glucose
Sucrase	Sucrase	Sucrose \longrightarrow glucose + fructose
Lactase	Lactase	Lactose \longrightarrow glucose + galactose
Lipase (steapsin)	Lipase	Fat \longrightarrow glycerol + fatty acids
Trypsinogen (yields trypsin)		(1) Chymotrypsinogen \longrightarrow chymotrypsin
		(2) Protein and peptides hydro- lyzed at internal bond
Chymotrypsinogen (yields chymotrypsin)		Hydrolyzes certain amino acids from end of protein chain
Erepsin group (polypeptidases)	Erepsin group (polypeptidases)	Specific amino acids removed by specific enzymes
	Enterokinase	Trypsinogen \longrightarrow trypsin
	Nuclease	Nucleic acid \longrightarrow
	Nucleotidases, etc.	4 Nucleotides \longrightarrow
		H_3PO_4 + Nucleoside \longrightarrow
		Sugar + purine or pyrimidine

The proteolytic enzymes deserve comment, since there is a large number of them. The group of enzymes formerly called "erepsin" has been partially separated and some of the individual enzymes crystallized. Thorough study indicates that many of these enzymes have a specific function, for example, the hydrolysis of a terminal lysine or arginine when it is attached to a polypeptide through its carboxyl group. The multiplicity of these enzymes insures an efficient digestion of all protein under normal conditions.

Bile

The bile, which pours out of the duct of Henley from the gall bladder when chyme enters the intestine, is a yellow green fluid

with a pH between 7 and 8. It is continuously formed in the liver and stored in the gall bladder in concentrated form. It contains bile salts, bile pigments, salts particularly of Cu, Fe, Mg, Ca, Mn, and sterols. The bile pigments which are derived from the prosthetic portion of hemoglobin are evidently purely excretory products. The bile salts are salts of compounds such as taurocholic acid and glycocholic acid. These are products of taurine ($NH_2CH_2CH_2SO_3H$) and cholic acid which is related to cholesterol, or of glycine and cholic acid. The bile salts are particularly important in the digestion of lipides, since (1) they act as emulsifying agents for the lipides in water. In the digestion of lipides there must be an intimate contact between the lipide, the enzyme, and the water. On emulsification the surface of lipide is increased many thousand-fold. The bile salts also have (2) an additional accelerating effect on the rate of hydrolysis of fats. (3) The absorption of the fatty acids produced in digestion fails completely unless bile salts are present. The mechanism of this reaction is not known although some hypotheses have been advanced. The fact that so much of our food contains a small film of fat accounts for (4) the impairment of digestion of carbohydrates and proteins which occur when bile secretion is blocked or diminished.

Another function of the bile is (5) in the absorption of some of the fat-soluble vitamins: the carotenes (provitamin A), vitamin K, and probably vitamin D. In adults, a vitamin K deficiency is only encountered when the bile duct is obstructed either through gallstones or inflammation.

Bile Functions

1. Emulsification of fats.
2. Absorption of fatty acids.
3. Acceleration of hydrolysis by lipase.
4. Increased absorption of some vitamins.
5. Channel of excretion.
6. Indirectly influences digestion of carbohydrates and protein.

Absorption

The mucosa of the intestine has many folds and ridges and is covered with many small fingerlike projections called villi. The

surface of the mucosa is consequently very large; for an adult it is estimated that it is about 10.5 square meters. The movement

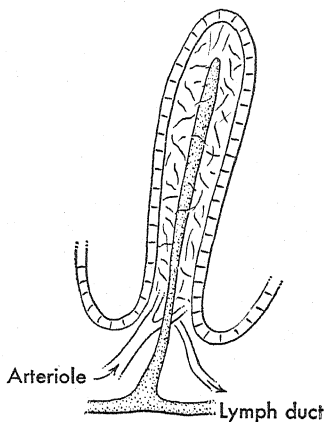


Fig. 26-5. A villus of the intestine. Each villus is richly supplied with blood vessels into which many of the products of digestion and soluble foodstuffs pass. A lacteal is connected to a lymph duct. Most of the fat is carried into the body through this system.

of the intestine brings the contents in close and frequent contact with the cells lining the intestine and there is consequently great opportunity for the absorption of the products of digestion and other small molecules. The means by which absorption is accomplished, the factors which influence it, and the changes which occur are only partially understood. It is known that osmotic pressure alone cannot account for the rapid and efficient absorption of a small molecule such as glucose. The enormous power of absorption of the intestine has been demonstrated in observations on a man with only 3 feet of intestine instead of the normal length (surgically removed) who absorbed 70 per cent of the protein and all carbohydrate ingested (Todd, Ditterbrandt, Montagne, and West). The small molecules of carbohydrate (glucose, galactose, and fructose) and the amino acids are absorbed and transferred directly to the blood capillaries with which the intestine is richly supplied. Fatty acids and glycerol appear to be absorbed by the intestinal cells under the influence of bile salts and there synthesized into phospholipide and neutral fat. These lipides are then passed on to the lymph ducts and carried in the lymph through these ducts until the thoracic duct joins the blood system. A small part is absorbed directly into the blood stream.

Feces

The semifluid material which passes into the large intestine (colon) through the ileo-caecal valve contains little of the original food capable of digestion. Seeds, fruit skins, cellulose, etc., are present, as well as some of the substances secreted in the digestive fluids and the mucin poured out all along the gastro-intestinal tract. During the rather long stay in the colon, water is absorbed until the mass is semisolid, and extensive changes in other molecules are brought about by the many bacteria which inhabit the large intestine. The bacterial products include a mixture of gases which make up the intestinal flatus: carbon dioxide, ammonia, methane, hydrogen sulfide, hydrogen, and methyl amine; some organic acids such as acetic and butyric; and some amines which impart to the feces their characteristic fetid odor. (These amines were once considered the source of symptoms of constipation since they are poisonous when injected into the blood. There is now little support for the idea that they may be absorbed from the colon and that "auto-intoxication" can occur. Alvarez was able to demonstrate that the symptoms of constipation may be produced by packing part of the large intestine with sterile cotton.) The feces contain (1) these products of bacterial action as well as (2) indigestible material, (3) secretions from the alimentary tract, (4) water and

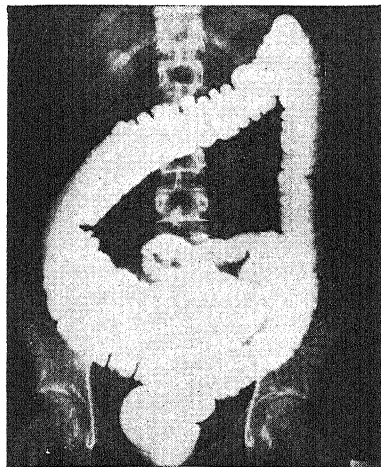


Fig. 26-6. X-ray of the large intestine following a barium sulfate enema. The ascending, transverse colon, and descending colon, as well as the rectum, are plainly visible. Some of the barium sulfate has passed into the lower part of the ileum. Notice the shadows of the rib and their relationship to the transverse colon. (Courtesy of Jackson, Hildreth, Volderauer & Pearson, Radiologists.)

(5) bacteria, living and dead. These bacteria make up one-fourth to one-half the dry weight of the feces.

DIGESTIBILITY

The term "digestibility" is sometimes used to describe the ease or comfort with which a food is digested. Usually, however, it refers to the coefficient of digestibility which is equal to the difference between the amount of a constituent present in the food expressed as 100 per cent and that present in the feces.

$$\text{Coef. of digestibility} = \text{Ingested (100\%)} - \% \text{ in feces}$$

For example, if the food contains 40 grams of lipide, and the feces from this food (they may be marked by ingesting at the same time an indigestible dye such as carmine) contain 2 grams of lipide, the coefficient of digestibility will be:

$$\text{Coef. of digestibility} = 100\% - (2/40 \times 100)\% = 95\%$$

Atwater has conducted hundreds of experiments and finds that for a mixed diet the coefficients of digestibility for various food is:

Carbohydrate	98%
Lipide	95%
Protein	92%

This data does not indicate that 8 per cent of the protein escapes digestion, although it does mean that the average gain to the body from protein is only 92 per cent. On a protein free diet, there may be 0.5 to 0.9 gram of nitrogen in the feces per day. This is more than is frequently present on a diet adequate in nitrogen. The 8 per cent probably represents nitrogen excreted in the digestive fluids since, you will remember, both the enzymes and the mucin are proteins.

External factors have little effect on the coefficient of digestibility.

NEW TERMS

Enzyme, saliva, gastric digestion, intestinal mucosa, bile, bile salts, bile pigments, feces, flatus, coefficient of digestibility.

QUESTIONS

1. Describe the gastro-intestinal tract and its adjuncts.
2. What digestive fluids are produced along the gastro-intestinal tract? Which contain enzymes?
3. Where are the salivary glands located? What is the composition of saliva? Does it contain any enzymes? What are their functions?
4. How long does salivary digestion persist? Why does it cease when gastric juice is mixed with the food and saliva?
5. What are the functions of the stomach? Explain why the pH of gastric juices rises when food is mixed with it.
6. Give the course of the reactions which are catalyzed by the enzymes present in gastric juice.
7. What enzymes are present in pancreatic juice and intestinal juice? What reactions do they catalyze?
8. What is the composition of the material which flows into the large intestine? Which is excreted in the feces? What changes take place in the large intestine?
9. What is the flatus? Is it normally formed? What is the source of the various gases that compose it?
10. Calculate the coefficient of digestibility of a protein if the ingestion of 120 grams resulted in feces which contained 9.6 grams of protein.
11. What are the products of digestion of sucrose? Where does sucrose occur in the gastro-intestinal tract? How are the products of digestion absorbed?
12. Trace the digestion of a protein through the gastro-intestinal tract, enumerating all the enzymes which influence protein digestion and products of the action. How are amino acids absorbed?
13. What are the products of fat digestion? How are they absorbed? What factors influence fat absorption?

Fat Metabolism

Metabolism includes all the chemical changes which molecules undergo from the time they are absorbed until they are excreted. *Anabolism* includes the chemical reactions by which tissue components are synthesized and *catabolism* the reactions by which these large molecules present in tissues are broken down.

You will remember that when fat is absorbed and carried through the lymph system, neutral fat and phospholipides are synthesized. There is little free fatty acid or glycerol in the lymph. The lymph returns to the blood circulation and carries these lipides into the circulation with it.

In this chapter only fat metabolism will be discussed, although phospholipide metabolism is intimately connected with fat metabolism. It must be remembered that phospholipides are very closely related to fats chemically.

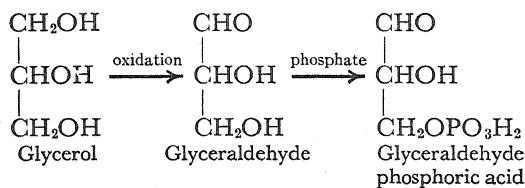
The fate of fat in metabolism may follow one of the following courses:

1. Synthesis into needed compounds, phospholipides, glycolipides, etc.
2. Oxidation to CO_2 and H_2O .
3. Storage, particularly in adipose tissue.

OXIDATION

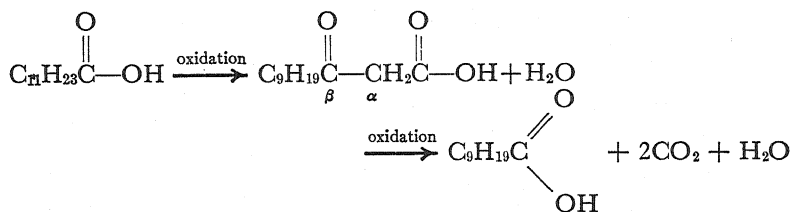
You have probably heard frequently that the function of fat in the body is to be "burned for energy." You have recognized that in some way the fat molecules are changed into carbon dioxide and water and that this chemical process is accompanied by the release of energy. Exactly what happens to the molecules of fat as they are oxidized in the body has been difficult to discover. It is now known that fat is oxidized by one primary path and probably by several others in small amounts. The path by which most of the fat molecules are oxidized will be studied.

The oxidation of a molecule of fat in the body follows two paths, the glycerol portion of the molecule taking one path and the fatty acids portion the other path. The glycerol is oxidized in a manner similar to carbohydrate oxidation which you will study in Chapter 29. It is first oxidized to glyceraldehyde and then esterified with phosphate to glyceraldehyde phosphoric acid.



The glyceraldehyde phosphoric acid may be oxidized to pyruvic acid and then by the regular cycle to carbon dioxide and water. Or this compound may be synthesized into glycogen by a reversal of the reactions which take place when glycogen is catabolized. It has been demonstrated that liver cells will use glycerol for the formation of liver glycogen. The third possible fate of this molecule derived from glycerol is conversion to a nonessential amino acid.

Fatty acids are oxidized according to a scheme called beta-oxidation. During the past forty years considerable evidence has accumulated to indicate that the principal method of oxidation of fatty acids is two carbons at a time, with oxidation occurring on the beta (second from carboxyl) carbon. You will remember that all fatty acids found in nature have an even number of carbon atoms except propionic $\text{C}_2\text{H}_5\text{COOH}$ and valeric $\text{C}_4\text{H}_9\text{COOH}$.

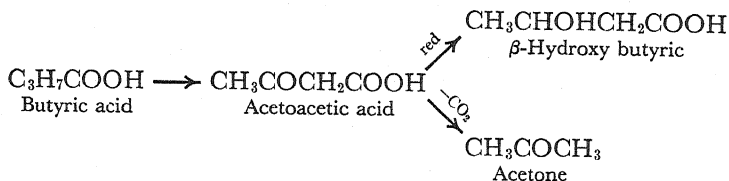


Total path:



If you look at this series of fatty acids carefully, you will notice that all of them have an even number of carbon atoms. Each step is accomplished by intermediate steps in which the beta carbon is oxidized and the carboxyl carbon and the alpha carbon then removed. Water is produced in the first oxidation in each case and water and carbon dioxide in the second oxidation. Energy is liberated in the series of reactions. Both products are excreted by way of the lungs, while water is also excreted in urine, sweat, and feces.

When fatty acid oxidation is incomplete, *acetone bodies* accumulate in the blood and are excreted in the urine. These are acetoacetic acid, $\text{CH}_3\text{COCH}_2\text{COOH}$; beta-hydroxybutyric acid, $\text{CH}_3\text{CHOHCH}_2\text{COOH}$, which may be obtained from acetoacetic acid by reduction, and acetone, CH_3COCH_3 , which may be obtained from acetoacetic acid by decarboxylation.



Butyric acid is produced in the oxidation of all fatty acids by the degradation of the acids two carbons at a time. On normal oxidation of butyric acid, acetoacetic acid will be formed. This is shown in the diagram. Normally the acetoacetic acid is oxidized to acetic acid, CH_3COOH , carbon dioxide and water. Incomplete oxidation of fatty acids occurs under conditions such as: uncontrolled diabetes mellitus, starvation or a very high fat diet (ketogenic diet). The cause of the incomplete oxidation is interpreted in one of two ways: (1) some investigators believe that the oxidation of carbohydrate is essential to the complete oxidation of fat. They say, "Fat burns in a flame of carbohydrate." In uncontrolled diabetes and in starvation, carbohydrate metabolism is much curtailed, and they conclude that it is insufficient for complete oxidation of fatty acids. (2) Other investigators consider the ability of the body to oxidize fatty acids limited. When small amounts of fat are oxidized, it is possible for the fatty acids to be oxidized completely, but when the quantity is increased, the body can no longer oxidize the

fatty acids completely. In starvation and diabetes, oxidation of carbohydrate is limited, and the oxidation of fat and protein is consequently increased to meet the body's needs. Under these conditions the maximum for complete fatty oxidation is exceeded and oxidation of some molecules stops at acetoacetic acid, instead of being carried to carbon dioxide and water.

STORAGE

There are apparently two types of depots for fat, one in the adipose tissue, which disappears quite quickly during starvation, and one supporting organs such as the kidney, which is quite stable. Some fat is present in the body even in undernutrition, but it is only when the diet contains more calories than the body's requirement that a considerable accumulation of fat occurs. Then the quantities may be strikingly large. The fat may be formed when the diet is high in fat, high in protein, or high in carbohydrate.

This observation indicates that fat may be synthesized from either carbohydrate or protein, and all controlled experiments have supported this conclusion.

The type of fat stored may be influenced by the composition of the diet. When the diet is high in carbohydrate, the fat deposited is characteristic of the species. Thus the fat of hogs fattened on high carbohydrate is low melting, while that of steers and sheep is high melting. This difference is noticeable when fat from meat runs out on a platter, since that from beef and mutton solidifies readily. You will recall that the melting point of a fat reflects its chemical constitution. Fat is an economical storage form since it contains 9 calories per gram whereas carbohydrate contains only 4 calories per gram.

When animals are stuffed with a diet moderately high in fat, the fat stored is intermediate in composition between diet fat and the typical body fat. The body is capable of carrying out some saturation and desaturation of fatty acids. Schoenheimer and Rittenberg have fed esters of fatty acid containing deuterium to mice. These fatty acids containing usually two atoms of the isotope of hydrogen are chemically and, therefore, metabolically indistinguishable from ordinary fatty acids. When tagged

saturated fatty acids were fed to the mice, it was found that unsaturated as well as saturated fatty acids containing deuterium were stored. When unsaturated deuterium fatty acids were fed, again unsaturated as well as saturated fatty containing deuterium were stored. This indicates that saturation and desaturation reactions can occur in the body. Schoenheimer and Rittenberg have evidence that the site of the transformation is the liver. Other observations indicate that when phospholipide is synthesized during absorption, there is some change in the fatty acid makeup compared with that of the food. It has been suggested that fatty acids from the body are utilized in this reaction and that the product, consequently, begins to resemble characteristic body fat.

When an animal is overfed a diet high in fat, the body can no longer carry on the saturation and desaturation reactions at a rate rapid enough to affect the stored fat. Dogs have been fed large quantities of rape seed oil until large depots of soft flabby fat were built up, while others deposited a hard fat on a diet high in mutton tallow. When the culture of soybeans began to spread through the midwest, there was some pork produced with low sales value. The hogs were fattened on soybeans, high in a liquid fat, and the fat of the pork had a very low melting point. Human beings do not ordinarily consume such high fat diets.

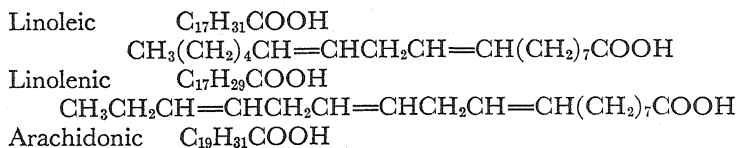
Although most phenomena and conditions in nature are found to be dynamic, many scientists formerly considered the storage of fats as static. They believed it was the sort where fat was tucked into adipose tissue much as money might be into a sock, and there it stayed until a particular process forced its withdrawal. Using deuterium fatty acids, Schoenheimer and Rittenberg disproved this theory. They found that if an animal were fed an adequate diet containing deuterium fatty acids, no increase in weight would occur, but deuterium fatty acids were deposited. If the feeding of the deuterium fatty acids ceased, these acids would gradually disappear from the fat stores, although the stores were not changing in quantity. These observations could only mean that the stored fat is very labile. Even where the quantity of fat is not changing or increasing, some of that fat is disappearing from the depot and being replaced by fat from the diet or from synthesis.

FAT SYNTHESIS

The synthesis of fat in the body appears to be a continuous process. Not only is fat synthesized from the fragments of food fat which are produced during digestion, but it is also synthesized from non-fat compounds. Glucose is readily changed into fat in the body. The widely held idea that "carbohydrates are fattening foods" is entirely correct. Likewise amino acids may be converted into fat. Numerous studies with laboratory animals have shown that if the animal can be induced to eat large amounts of a diet high in carbohydrate or a diet high in protein, rapid increase in the fat depots occurs. Even in an animal or man who is not gaining weight and is not increasing the amount of fat in his body, fat synthesis occurs constantly. However, if the rate of withdrawal of fat from the depots is as rapid as fat synthesis, then no gain occurs.

ESSENTIAL FATTY ACIDS

In 1929 Burr and Burr reported their observations on the effect of a fat-free diet on rats. They found that the animals developed a scaly skin with much dandruff in the fur and a scaly, ridged tail; the animals became very thin; hematuria (blood in the urine) and albuminuria (albumin in the urine) appeared, followed by death from kidney damage. In the females ovulation was irregular and in the males a lack of sex interest occurred. The preventative or curative effect of some natural fats was at length traced to the presence of at least one of three fatty acids:



Although the liver is able to desaturate fatty acids, it evidently is unable to synthesize these acids.

Because one of the outstanding symptoms of a fatty acid deficiency in rats is a scaly skin, some cases of persistent eczema in humans have been suspected of being just such a deficiency. There have been a few reports of a low level of unsaturated fatty acids in the blood of these patients as well as reports of

successful treatment with fats of high unsaturated fatty acid content. An attempt to produce an experimental unsaturated fatty acid deficiency in an adult man was unsuccessful after six months of a low fat diet. Although the blood unsaturated fatty acid level decreased 30 per cent, no symptoms developed. It is likely that there is a requirement for unsaturated fatty acids by human beings, but this has not been proved.



Fig. 27-1. Fatty acid deficiency in the rat. Notice the scaly tail and foot. (Courtesy of Dr. George O. Burr.)

NEW TERMS

Metabolism, anabolism, catabolism, beta-oxidation, acetone bodies, fat depots, essential fatty acids.

QUESTIONS

1. How does fat reach the general circulation after being absorbed from the intestine?
2. How is glycerol oxidized in the body?
3. What is the major path for the oxidation of fatty acids? Under what conditions is fatty acid oxidation incomplete? What are the products of incomplete oxidation? Show by equations how these products are formed.
4. What substances, other than fats, may be transformed into fats and stored in the fat depots of the body?
5. Is there a turnover in the fat in our fat depots when our body weight is stationary or does it "stay put"?
6. How does the composition of the diet influence the composition of body fat? Is this significant in man?
7. What are the essential fatty acids? What are the deficiency symptoms in rats fed a diet devoid of them? Are they essential for man? What is the evidence?

Protein Metabolism

Amino acids are produced in digestion and absorbed in the blood stream. These and the amino acids produced from the catabolism of tissue protein may undergo the following fates: (1) synthesis to protein, (2) deamination, and (3) very small amount of storage.

SYNTHESIS OF PROTEIN

In order for a molecule of protein to be synthesized, it is necessary that all the amino acids be supplied. Some of these amino acids may be synthesized in the body, but others must be present in the diet. These amino acids which cannot be synthesized in the body are called *essential amino acids*. *They are defined as amino acids which cannot be synthesized in the animal organism from materials normally present in the diet at a rate sufficient for normal growth.* (In adults the determination depends on nitrogen balance.)

An awareness of the existence of essential amino acids first developed about forty years ago from the studies of Osborne and Mendel on the nutritive value of proteins. They fed simple diets, containing only one protein, to young rats and measured their growth. Some rats grew at a normal rate, others slowly, and others grew thin and listless and then died. The difference in the nutritive value of these proteins was shown to be in their amino acid makeup. The "complete proteins" which supported normal growth contain all the essential amino acids and in goodly amounts. The "incomplete proteins" on which animals sickened and died were lacking in one or more of the essential amino acids. The subject was further studied and finally in 1935 good growth of young rats was produced on diets containing no protein and only ten amino acids: lysine, histidine, leucine, isoleucine, phenylalanine, tryptophane, methionine, valine, threonine, and arginine.

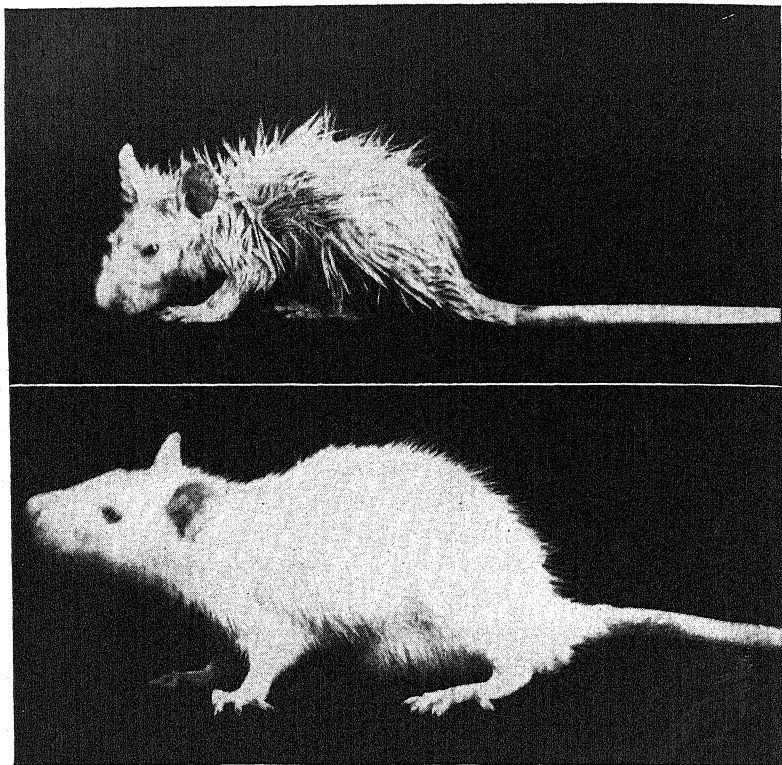


Fig. 28-1. Amino acid deficiency in rats. This rat was fed a diet adequate in everything except the amino acid, valine. The top picture shows his appearance after 28 days. Valine was then added to his ration and he returned to normal weight and health. The bottom picture was taken 25 days after the inclusion of valine in the diet. (Courtesy of W. C. Rose, S. H. Eppstein, and the Journal of Biological Chemistry.)

When one of the first nine was dropped out of the diet, the animal died. Arginine was a little different in that although its omission caused a marked deceleration in the rate of growth, it did not cause death. Evidently the rat can synthesize arginine but at a rate too slow for normal growth.

More recently adult men have been fed diets containing no protein and only a few amino acids. The adequacy of this ration has been tested by the nitrogen balance study explained below. It has been shown that they require only eight amino acids: lysine, tryptophane, leucine, isoleucine, phenylalanine, methio-

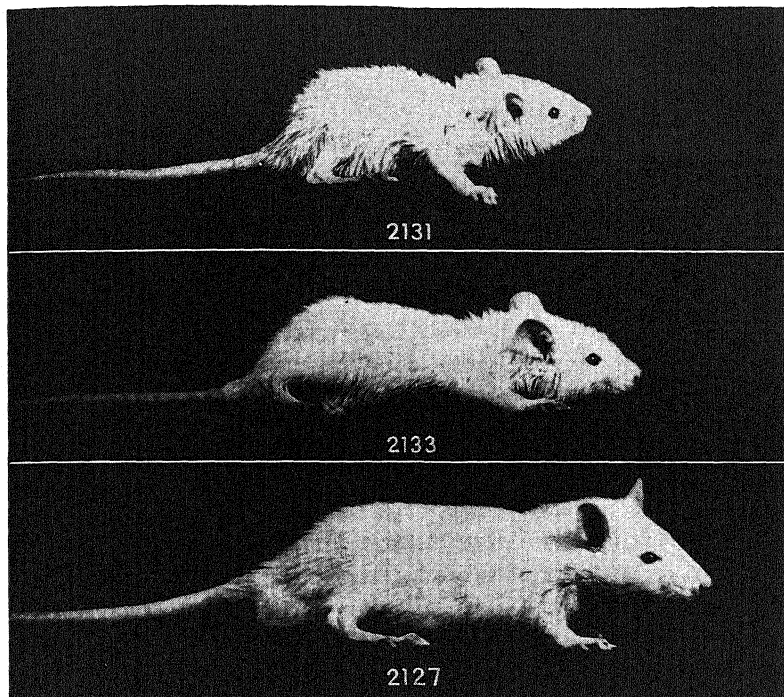
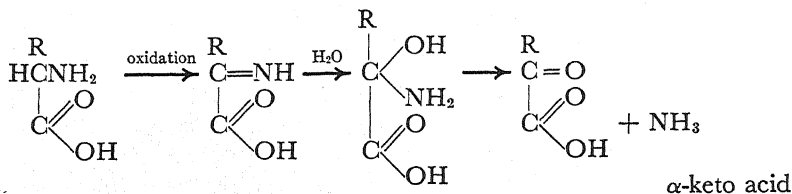


Fig. 28-2. Essential amino acids. These three animals were litter mates and had been on the experimental diet 23 days. Rat 2131 received isoleucine and norleucine; rat 2133 received leucine and norleucine; rat 2127 received leucine and isoleucine. Leucine and isoleucine are essential amino acids for the rat. (Courtesy of Drs. W. C. Rose and M. Womack.)

nine, valine, and threonine. If one of these is omitted from the diet, a negative nitrogen balance occurs.

DEAMINATION

Experiments on amino acid metabolism indicate that the amino acids follow the following series of reactions:



The alpha-keto acids, with the exception of that corresponding to lysine, may be resynthesized to amino acids, probably by the reversal of this series of reactions. They may also be oxidized to produce CO_2 , H_2O , and energy or transformed into fat or carbohydrate (about 57 per cent of amino acids), although the pathway depends on the nature of the R groups.

The ammonia undergoes a series of reactions (ornithine cycle) and is transformed into urea:



This is excreted in the urine. Other molecules containing nitrogen which appear in human urine are uric acid and creatinine.

PROTEIN REQUIREMENT

The protein requirement for human beings has been estimated by the nitrogen balance study. A balance study is an investigation of the difference between the amount of a nutrient ingested and the amount excreted.

$$\text{Balance} = \text{Amount ingested} - \text{Amount excreted}$$

When the balance is 0 (equilibrium) the amounts ingested and excreted are equal and there is neither loss nor storage of the nutrient. When the balance is negative, loss to the body is occurring, while when the balance is positive, storage is occurring. When the nitrogen balance is studied, the ingested nitrogen must be determined in the protein and amino acids of the food.

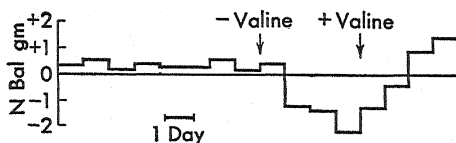


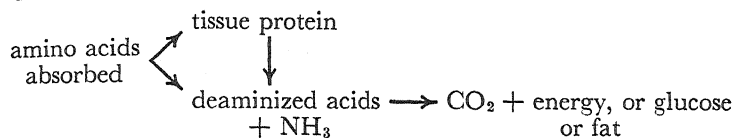
Fig. 28-3. The effect of an essential amino acid on nitrogen equilibrium in man. When valine is dropped out of the ration the subject goes into negative nitrogen balance.

But when the amino acid is restored to the ration there is a short period of positive nitrogen balance. This demonstrates that valine is essential for man. (Courtesy of Drs. W. C. Rose, J. E. Johnson, W. H. Haines, and the Journal of Biological Chemistry.)

Excreted nitrogen is nitrogen in urea, creatinine, protein in urine and feces. (Sweat is not quantitatively important.) As long as the ration is adequate both as to amounts and kinds of amino acids, the balance will be at equilibrium in an adult

(slightly positive during growth), but when it is inadequate the balance becomes negative.

Simplification of protein metabolism shows the following few important relations.



Amino acids which are not used for tissue protein or such specialized syntheses as thyroxine, an amino acid derivative, are deaminized and the nitrogen is excreted as a urinary product. Along with this nitrogen there is some from tissue protein catabolism. In an adult where tissue protein anabolism just equals catabolism, there is therefore equilibrium. If, however, the amino acid composition is such that protein anabolism cannot occur, then most of the nitrogen absorbed is excreted PLUS the nitrogen from protein catabolism. The balance is now negative.

Studies of this type on mixed diets give an indication of the quantity of protein necessary for maintenance of the body, while studies with diets containing only pure amino acids give an indication of the essentiality of certain amino acids. The recommendation of the committee on Food and Nutrition of the National Research Council (1941) allows at least a 50 per cent margin of safety above the quantity necessary for balance. This is good dietetics since a "mixed diet" varies considerably in its amino acid composition, and our diet patterns likewise vary from day to day. This committee has recommended 70 grams of protein for a 70-kilogram man and 60 grams for a 56-kilogram woman or approximately 1 gram per kilogram body weight for adults. In pregnancy the recommendation is increased 25 per cent and in lactation where protein synthesis is very rapid since much is secreted in the milk, it is increased by 67 per cent. In children where the demands of growth must also be supplied, it is recommended that infants ingest 3 to 4 grams per kilogram with the amount per unit weight decreasing as the rate of growth decreases.

STORAGE

The storage of proteins or amino acids in the body is almost impossible. There has been a report of a slight increase in liver

protein when the diets of rabbits were increased from adequate to very high protein.

NEW TERMS

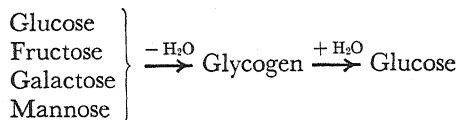
Deamination, essential amino acids, balance study, equilibrium, positive and negative nitrogen balance.

QUESTIONS

1. Explain how body protein is maintained. Why are the essential amino acids so important to this process? What is the source of the nonessential amino acids?
2. How is it possible to demonstrate in rats that a particular amino acid is essential? In man?
3. What is a nitrogen balance study? What is the significance of a negative nitrogen balance?
4. How much amino acid storage can be expected in the body? What implications does this have for good nutrition?
5. Explain the path of catabolism of amino acids. What happens to the nitrogen? How is it excreted?
6. What is an alpha-keto acid? How is it formed in metabolism? What is its fate?

Carbohydrate Metabolism

The carbohydrate molecules which are present in food or produced in digestion are glucose, fructose, galactose, and very small quantities of mannose. These are absorbed and carried by the blood capillaries to the general circulation. The portal vein collects the blood from the intestines and disperses it through the liver while arterial blood is supplied the liver through the hepatic artery. All blood then leaves the liver through the hepatic vein. As the blood flows through the liver, the carbohydrate molecules present in the blood are partially removed by the liver cells and changed into the polysaccharide, glycogen. Although glycogen is a glucosan and forms glucose on hydrolysis, it may be formed from fructose, galactose, and mannose as well as glucose. The liver cells may remove any monosaccharide which is produced in digestion and carried by the portal blood, to produce glycogen.



When there is a rapid absorption of carbohydrate from the intestine, the blood issuing from the hepatic vein will still have considerably more carbohydrate dissolved than blood during fasting. The liver cells remove carbohydrate but soon after a meal, the rate of absorption is so high, they cannot immediately remove all of it (see carbohydrate tolerance curve) from the circulating blood. The amount of carbohydrate in the blood, all through the body, therefore increases. Then gradually the level of blood carbohydrate falls back to that of the fasting state.

Not only is carbohydrate removed from the blood by the liver but some of the carbohydrate is withdrawn by muscle cells to

form muscle glycogen; some may be stored in skin; or if the concentration is very high (above 160 to 170 milligrams per 100 milliliters of blood for most adults), it will be excreted in the urine. These losses finally lower the carbohydrate content of the blood to the fasting level.

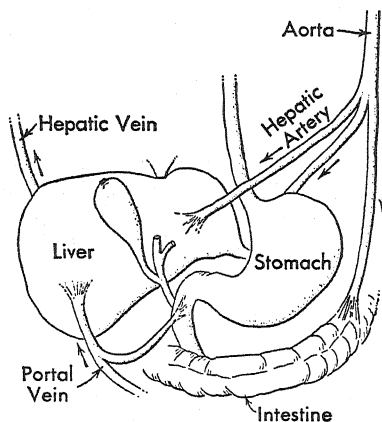


Fig. 29-1. Diagram of circulation of blood to liver, stomach, and intestines. The arteries divide into capillaries which supply the tissues with nutrients and remove waste products. The capillaries then form larger and larger veins which carry blood away from the tissues.

If no more food is eaten, the blood from the intestine will, after a fairly short time, cease to add carbohydrate to the circulation. The removal of glucose by the muscles and tissue will continue and will tend to lower the blood glucose level to the

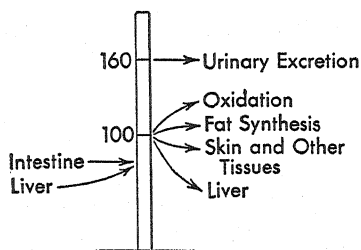


Fig. 29-2. Maintenance of blood glucose level. Glucose is added to the blood during adsorption or between meals by the release of glucose from the liver. Glucose is lost from the blood stream by absorption by the tissues and consequent oxidation, by transformation into glycogen in the liver, by fat synthesis, and, when the level in the blood exceeds the renal threshold, by excretion.

fasting level. If, after digestion is complete, samples of blood are removed and analyzed from time to time, it will be found that the glucose level is remarkably constant. The liver glycogen is rapidly changed into glucose and thus maintains the blood glucose level.

The great facility of the liver cells to form glycogen from glucose and other monosaccharides when the blood level is high,

and to form glucose from glycogen when there is a danger that the blood level is falling are under the control of a number of hormones. Two of the most extensively studied are insulin and adrenalin.

HORMONES IN CARBOHYDRATE METABOLISM

Insulin

Insulin is a hormone produced in the pancreas and poured directly into the blood stream. It is a protein of relatively low molecular weight (35,000 to 41,000) that is unique in containing only a small number of amino acids.

Injection of insulin into an animal causes a decrease in blood glucose and increase in liver glycogen and an increase in tissue

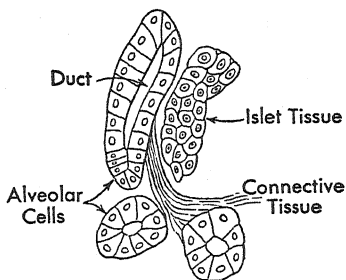
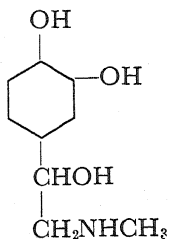


Fig. 29-3. Section of the pancreas. The alveolar cells produce pancreatic juice which flows out into the intestine while the islet tissue produces insulin which flows into the blood.

respiration. It is inferred from these observations that insulin stimulates the transformation of glucose to glycogen in liver cells and represses the transformation of glycogen to glucose. Other cells of the body increase their metabolism of glucose through the influence of insulin.

Adrenalin (epinephrin)

Adrenalin is a hormone produced by the adrenal glands. It is an amine with the formula



When it is injected into an animal the blood sugar rises, the liver glycogen decreases, and tissue respiration increases. This hormone appears to stimulate hydrolysis of glycogen (glycogenolysis) as well as tissue metabolism of glucose.

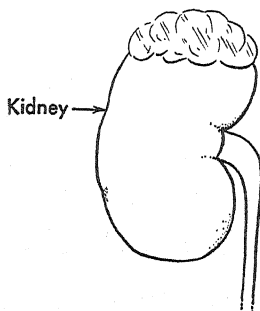


Fig. 29-4. The adrenal (or suprarenal) gland caps the kidney.

These two hormones do not comprise all the hormones which influence carbohydrate metabolism, but they will give you an insight into the carbohydrate tolerance curve. (Discussion of other hormones may be found in most extensive textbooks on biochemistry.)

CARBOHYDRATE TOLERANCE CURVE

The carbohydrate tolerance curve is a graph showing the changes in blood glucose after ingesting a standard quantity (frequently 100 grams or sometimes 1 gram per kilogram body weight) of glucose. It is worth studying because qualitatively the same changes occur in our blood stream after each meal. When the amount of carbohydrate absorbed is very great, the curve may rise higher and be stretched out, and when the amount of carbohydrate absorbed is small, the curve will be com-

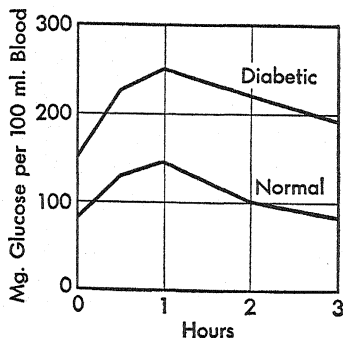


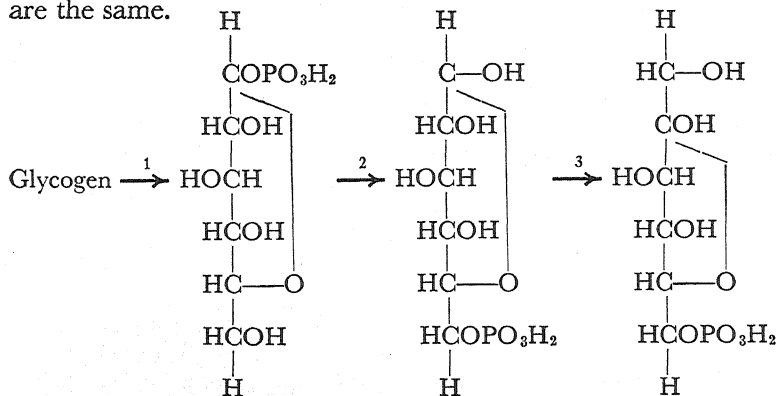
Fig. 29-5. Typical carbohydrate tolerance curves.

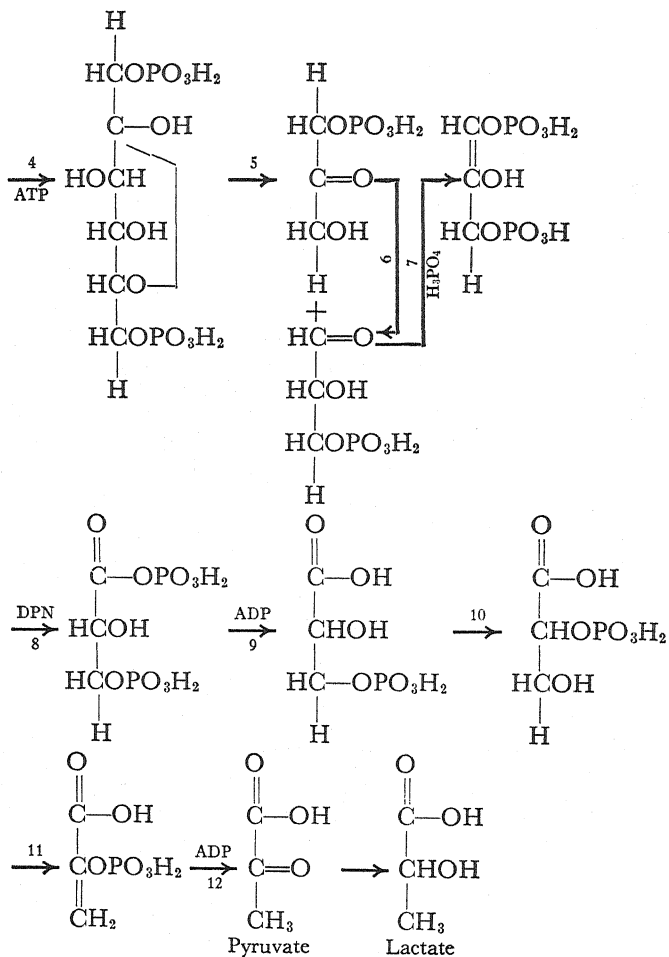
pressed. But considerable useful knowledge may be gained from an interpretation of the curve in terms of insulin and adrenalin.

During the first half hour after a meal the blood glucose level rises rapidly. This stimulates the pancreas to secrete more insulin, and the conversion of glucose to glycogen is accelerated. As absorption slows down, the blood glucose level falls until it at length reaches fasting level. But glucose is still being removed by the liver cells for the formation of glycogen, and the blood level consequently falls below fasting level. As this occurs, the adrenals pour out more adrenalin, some liver glycogen is hydrolyzed to glucose, and the blood glucose level is steadied at the fasting level.

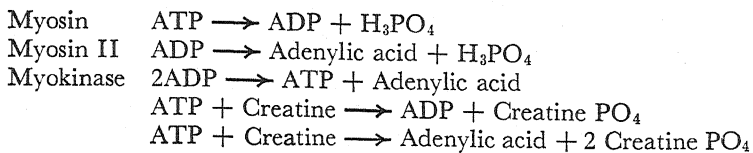
OXIDATION OF CARBOHYDRATE

The series of reactions which occur when either glucose or glycogen is oxidized is proving to be complicated in the number of reactions, the number of enzymes and coenzymes involved, and the number of interlocking reactions involved. Although a thorough study of the question is beyond the scope of this book, there is some value to be gained in a brief discussion of the topic. The student will get a picture of the complexity of biochemical reactions and the multiplicity of enzymes which must exist in an organism such as the human body. The series of reactions shows the probable path of oxidation of glycogen to pyruvic acid in tissue such as the contracting muscle. There is evidence that in some tissues such as brain, glucose is the starting material rather than glycogen. You will notice that of the twelve reactions given only two are nonenzymatic. Each of these ten enzyme systems is different, although some have prosthetic groups which are the same.





Other Phosphorylating Systems



ATP = Adenosine triphosphate

ADP = Adenosine diphosphate

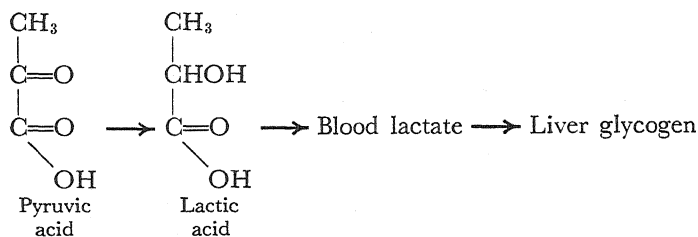
M = Metal

DPN = Diphosphopyridine nucleotide

Enzyme Systems

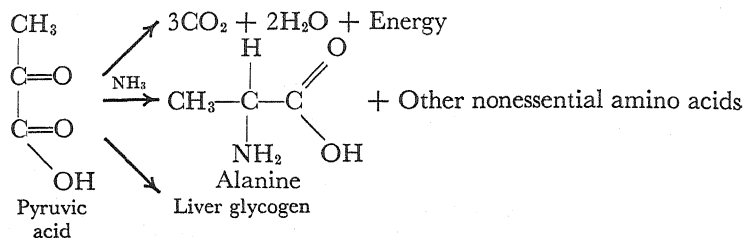
1. Phosphorylase (protein-Mg-adenylic acid)
2. Phosphoglucomutase (protein-Mg)
3. Isomerase (protein-M)
4. Phosphohexokinase (protein-ATP?)
5. Zymohexase (protein-M)
6. Isomerase (protein-M)
7. Nonenzymatic
8. Phosphoglyceraldehyde oxidase (protein-DPN)
9. Nonenzymatic
10. Triose mutase (protein-M)
11. Enolase (protein-Mg)
12. Phosphopyruvate phosphatase (protein ADP-Mg)

The primary reaction which occurs, then, in contracting muscle, appears to be a series starting with glycogen and ending with pyruvic acid. You may wonder how lactic acid fits in, since it is common knowledge that muscle fatigue is accompanied by increased lactic acid. Lactic acid appears to be a byproduct produced when the supply of oxygen is not sufficient to oxidize all the pyruvic acid produced. This condition occurs when there is vigorous muscular exercise. Some of the pyruvic acid is oxidized, but some is reduced to lactic acid. The lactic acid diffuses out into the blood stream and is carried to the liver where it may be converted to glycogen.



The pyruvic acid is oxidized one carbon atom at a time in the "citric acid cycle," or it may lose carbon dioxide to form acetic acid and then more carbon dioxide. The product of either action is three molecules of CO_2 which is excreted through the lungs. The pyruvic acid may undergo other fates as well as that

of oxidation. It may be converted to glycogen in the liver or it may be synthesized into nonessential amino acids.



VITAMINS AND CARBOHYDRATE METABOLISM

Vitamins are chemical compounds which must occur in the diet in order for normal health and life to be maintained. It can be deduced from this essentiality that our bodies are incapable of synthesizing these chemical compounds and that the vitamins are of prime importance in some metabolic reaction. For most of the vitamins there is no knowledge as yet as to their exact function. A few of the B vitamins have been shown to be important as coenzymes in certain steps in the series of reactions of carbohydrate metabolism. In step 8 of the series of reactions, the coenzyme is diphosphopyridine nucleotide, DPN, which accepts hydrogen from the carbohydrate fragment and thereby oxidizes it. The reaction does not occur unless the coenzyme is present. Part of this coenzyme is niacin, the antipellagra vitamin. If our diet is low in this vitamin, then carbohydrate metabolism is impaired. Two other vitamins which act as coenzymes at specific steps in the series are thiamine and riboflavin. Thiamine (vitamin B₁) prevents beri-beri in man and riboflavin prevents changes in the eye and skin. The exact spot where thiamine functions is in the disappearance of pyruvic acid. If the thiamine intake is low, pyruvic acid accumulates in the tissues and blood. It can be understood why these vitamins are essential to well being although they are required in very small amounts, since they operate in enzyme systems.

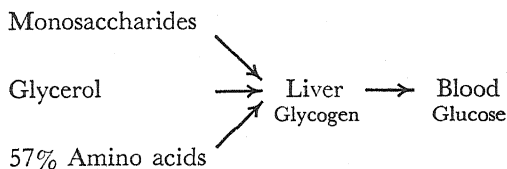
FAT FORMATION

It is common experience that carbohydrate ingested in excess of the energy needs of the body may be transformed into fat. In controlled experiments this has been shown to be true. Diets

very low in fat and high in carbohydrate have been fed to geese, dogs, and cows until they were very fat. It has been demonstrated that the amount of fat on the carcass plus that in the milk of cows is in excess of that ingested and that it arises from carbohydrate. In human beings this same transformation takes place readily when the calorie ingestion exceeds the need.

NUTRITIONAL REQUIREMENT

Most of our diets are high in carbohydrate, yet it is doubtful whether there is any real nutritional requirement for this group of foodstuffs. The liver can manufacture glycogen not only from monosaccharides but also from glycerol (present in fat) and about 57 per cent of the amino acids in proteins. Probably it is possible to live healthily on a diet low in carbohydrate. The blood glucose level must be maintained, glycogen and glucose are required for energy, but probably carbohydrate does not need to be present preformed in the diet.



However, from the standpoint of practical dietetics, a diet very low in carbohydrate is almost impossible. A well-balanced diet will contain a variety and a quantity of fruits and vegetables for their important supplies of vitamins and minerals, and most fruits and vegetables have considerable carbohydrate. A second consideration is the cost of diets. The cheapest group of foods is the cereal group, and this, too, is a group high in carbohydrate. The average American diet contains between 60 and 75 per cent carbohydrate. Nutritionists recommend that the protein level be adequate (it amounts to 10 to 15 per cent of the calorie value of the diet), the fat rather low, and that carbohydrate make up the rest of the energy need of the body. It has been reported, however, that animals on a carbohydrate-free diet do not thrive.

NEW TERMS

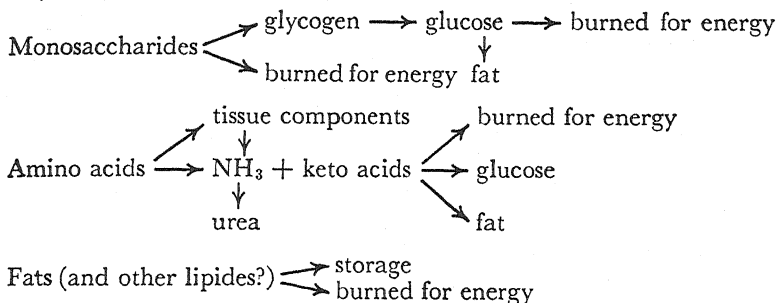
Carbohydrate tolerance test.

QUESTIONS

1. Trace the monosaccharides which are absorbed from the gastrointestinal tract through the body.
2. What happens to the monosaccharides which are removed from the blood by the liver cells? How is this removal influenced by insulin and adrenalin?
3. What carbohydrate is the normal constituent of the blood? How does the body maintain a normal amount of this carbohydrate in the blood during periods of fasting and between meals?
4. What chemical transformation occurs when carbohydrate is removed from the blood and deposited in the muscle fibers?
5. Explain how the carbohydrate tolerance test can differentiate a normal individual from a diabetic.
6. What is the primary source of energy in muscle contraction?
7. When is lactic acid (lactate) formed in large amounts in the contracting muscle?
8. How do some of the vitamins function in muscle contraction?
9. What happens to the oxidation of carbohydrate in the body when there is a deficiency of thiamine?
10. How extensive is the storage of carbohydrate in the body? What is the storage carbohydrate and where is it stored? What happens to carbohydrate which is eaten that is above the needs and storage capacity of the body?
11. What is the significance of carbohydrate in our diet? Is it possible that man could live on a diet devoid of carbohydrate? Is it practical? Why?

Energy Metabolism

The fates of the three main groups of foodstuffs in our bodies may be summarized as follows:



Eventually all these molecules are burned for energy. Therefore the general topic of *Energy Metabolism* will be discussed to learn a little more of the body's need for energy.

You will remember that chemical compounds possess potential energy and that part of this energy is released when they undergo exothermic reactions. *Energy metabolism* includes all the changes in energy which occur in the metabolic reactions in your body, in other words how much energy these compounds release or gain when they react in the cells of your body.

You eat foods which are rich in energy and you excrete compounds such as carbon dioxide and water which are poor in energy. There are both reactions which are exothermic and reactions which are endothermic occurring in your body. But the sum total when it is balanced up is exothermic. Primarily energy produced from the foodstuffs is used up.

ENERGY IN FOODS

Calorie

The potential energy in the food is measured in terms of the heat unit, the Calorie (see p. 32). The Calorie used in bio-

chemistry and nutrition in relation to man's energy metabolism, is the large Calorie, the kilogram calorie. (Unfortunately there is no consistency in capitalizing this Calorie to differentiate it from the small calorie.) The Calorie is defined as the quantity of heat which will raise the temperature of 1 kilogram of water 1° C. The number of calories of potential energy in a food may be determined by one of two methods.

Calorimeter

The direct method is one in which the food is burned in air or oxygen in a small metallic vessel, the bomb, and the heat released measured by submerging the instrument in a known volume of water and measuring the increase in heat. For example, if the bomb is submerged in 5 kilograms of water and the temperature rises 1° C., then 5 Calories have been liberated. Of course the increased temperature of the bomb must also enter calculations in a real determination. The series of chemical reactions which occur in the bomb are not the same as those which occur in metabolism, but when the starting material and the end products are the same, the overall energy exchange is the same. Thus when 1 gram of glucose is oxidized to CO_2 in the bomb, the same amount of heat, 4 Calories, is released as when 1 gram of glucose is oxidized to CO_2 during metabolism.

The only drawback to use of a bomb on foods, is that the nitrogen in protein is oxidized to NO_2 , while in metabolism it is not oxidized at all, but is removed from the amino acids as NH_3 . Thus for protein determinations the results with the bomb calorimeter are too high.

Oxycalorimeter

The oxycalorimeter is a device which measures the O_2 used and the CO_2 and sometimes H_2O produced by oxidation *in vitro*. Since the oxidation of a fixed quantity of a compound always yields the same number of grams of product as well as the same number of Calories, the number of Calories liberated can be calculated. The number of Calories of heat released can be correlated with the number of milliliters of CO_2 at standard conditions. The oxycalorimeter is supplied with a chart so that Calories can be directly read when CO_2 volume is known.

Chemical Analysis

Chemical analysis of foods containing carbohydrate, fat, and protein will give an estimate of the potential energy. Available carbohydrate yields approximately 4 Calories per gram in the body; fat 9 Calories per gram; and protein 4. Thus, if the amounts of these components are determined in a food, it is possible to calculate the approximate energy value of the food.

ENERGY EXPENDITURE

Energy is manifest in the body both as work and heat. The work is not only the work of muscles of arms and legs but the work of the internal organs, beating of the heart, contraction of diaphragm, maintenance of muscle tonus. The production of work energy is not a very efficient process (about 10 per cent efficient) so that it is accompanied by a great deal of heat. Increased work is accompanied by increased heat, as you are aware. In estimating the energy expenditure of an individual, consideration must be made of the basal metabolic rate, the expenditure for activity, and for specific dynamic action.

The *basal metabolic rate is the rate of energy expenditure when the body is at rest in bed, 10 to 12 hours after the last meal, in a warm room.* It is not the minimal energy expenditure of the body but it is the lowest waking expenditure and, therefore, is a convenient rate to measure. This represents the minimum energy expenditure to keep the body warm and maintain internal work. The basal metabolic rate may be determined either directly by a modification of the method of the bomb calorimeter or the modification of the oxycalorimeter. Since the apparatus necessary for the direct determination is very large and expensive, it is the oxycalorimeter which is commonly used in hospitals and clinics.

Variations in Basal Metabolic Rate

The basal metabolic rate varies from one individual to another with size, age, sex, and some other factors. The larger the animal, the higher the basal metabolic rate. There is not a very close correlation between basal metabolic rate and body weight or height, but a fair one between basal metabolic rate and surface area.

The variation in basal metabolic rate in calories per square meter with age and sex is well shown in Fig. 30-2. It will be noticed that the basal metabolic rate per square meter for girls always is lower than that for boys. At puberty there is a slight

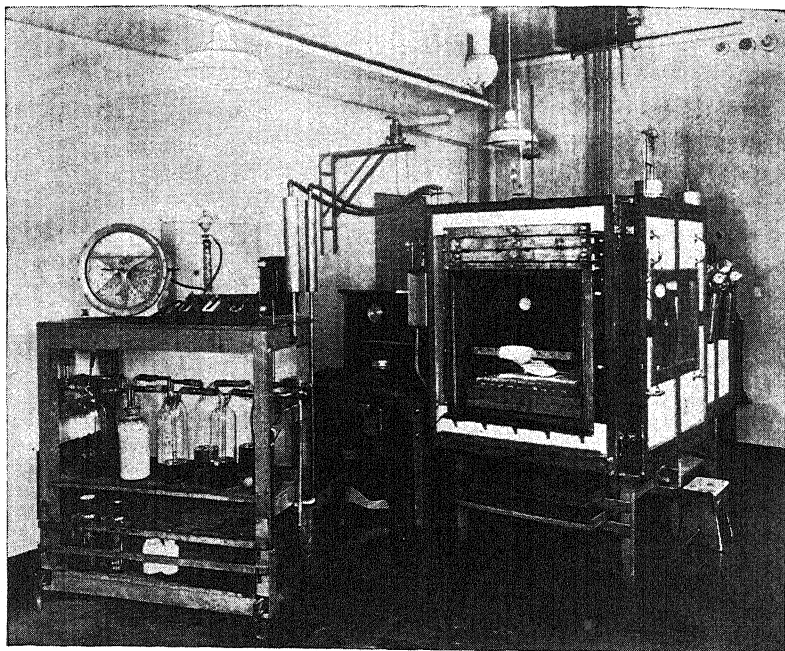


Fig. 30-1. Calorimeter for human being. The calorimeter is at right and is large enough to hold a man. It measures the heat produced in metabolism while the apparatus at left measures the carbon dioxide production. (Courtesy of Dr. Eugene DuBois.)

rise in the average rate, earlier in girls with the earlier puberty. In adulthood, women have a lower average basal metabolic rate per square meter than men. During adulthood there is a slow drop in the basal metabolic rate, so slow that it is very difficult to show from year to year. The variation between young and old men is, however, very marked.

The basal metabolic rate of an individual may change with changes in other factors than size, sex, and age. Emotions, changes in the rate of secretion of hormones, and pregnancy cause an increase or decrease in the basal metabolic rate. Fre-

quently the first determination of the basal metabolic rate is above normal, and yet when the determination is repeated, it is normal. The high first determination is probably the result of apprehension on the part of the subject with tense muscles, sometimes with rapid breathing and heart beat. This would result in an increased energy expenditure. The influence of emotions on the body is well known by everyone who has ever been angry or afraid. These emotions are accompanied by

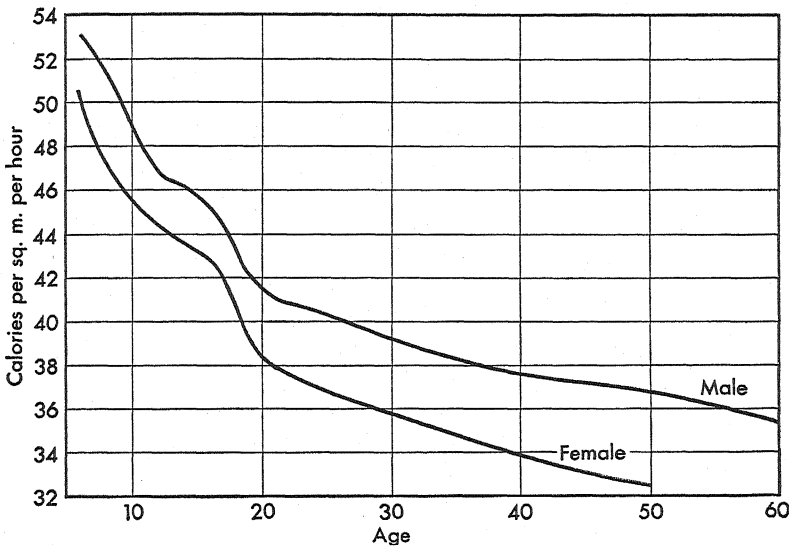


Fig. 30-2. Relationship of basal metabolic rate and age in male and female human beings. (Data taken from Boothby, Berkson, and Dunn, *Am. J. Physiol.*, 116, 468.)

great increases in energy expenditure. You can feel your heat production rise. The true basal metabolic rate cannot be determined during emotional stress.

The three glands of internal secretion most intimately connected with the basal metabolic rate are the thyroid, adrenals, and pituitary. When the hormone secretion from any of these glands is greater than normal (hyperthyroidism, hyperadrenalism, or hyperpituitaryism) the basal metabolic rate is increased. The pituitary is believed to have an indirect effect stimulating the thyroid and through it stimulating the basal metabolic rate.

It has been demonstrated that the pituitary produces a hormone (thyrotropin) which stimulates the thyroid. On the other hand, a secretion below normal (hypothyroidism, hypoadrenalinism, hypopituitarism) causes a decreased basal metabolic rate.

The effect is marked enough so that an abnormal BMR is one of the clinical signs that the thyroid and perhaps the pituitary are not functioning normally. Changes in the adrenals are not very common. The BMR is not the only clinical test a physician uses when he is trying to determine whether or not the thyroid is functioning normally, but it is of great value to him. The BMR is reported in terms of deviation from the normal. For example, one patient might have a +15% and another a -8%. A +15% would mean that the basal metabolic rate is 15 per cent above normal, while 8% means that it is 8 per cent below normal. Since the determination of the BMR cannot be accurately measured, a deviation of 10% (either +10% or -10%) is not considered significant.

During pregnancy the basal metabolic rate slowly rises. During the last trimester (seventh, eighth, and ninth months) when the fetus is growing rapidly, the BMR rises until it is approximately 20 per cent above normal. After delivery the basal metabolic rate of the infant (difficult to determine) plus that of the mother is about equal to the rate of the mother before delivery.

Activity

As soon as an individual rises from bed and begins to move about, his energy expenditure rises above the basal. If the basal rate is 1 Calorie per kilogram per hour, then the rate for sitting quietly is 1.4 Calories per kilogram per hour, an increase of 40 per cent, or for swimming is 7 Calories per kilogram per hour, an increase of 700 per cent. Mental activity does not increase the energy expenditure unless increased physical activity or tenseness is a byproduct of it. There have been measurements of the oxidative reactions in a nerve cell and the energy production but these are small in quantity. Compared to the needs for the basal metabolic rate and for activity, the needs for mental activity is very small and may be neglected in approximations of the body's total need.

Specific Dynamic Action

You have experienced on a hot summer day the feeling of warmth which occurs soon after eating. You have also experienced the warming effect of cold food like a piece of chocolate when you are chilled. *The extra heat which is generated when food is eaten is called specific dynamic action.*

The amount of heat produced depends on the number of calories consumed and the composition of the food. Protein has the greatest specific dynamic action — 30 Calories per 100 calories (25 grams) of protein, carbohydrate about 6 Calories per 100 calories (25 grams), and fat from 6 to 14 Calories per 100 Calories (11 grams). Usually for a mixed diet for each 100 Calories of food ingested, it is calculated that 6 Calories of extra heat are produced. The source of this heat has been variously explained and does not appear to depend on any simple reaction. It is not concerned with the digestive reactions, but rather metabolic ones.

The total energy expenditure then is the sum of several losses which can be measured or predicted. These are: (1) Basal metabolic rate, (2) activities, and (3) 6 per cent for specific dynamic action.

ENERGY BALANCE

If the food does not contain sufficient calories as potential energy to cover this expenditure, some of the body tissue is metabolized and not replaced and there is a loss of weight. If the number of calories ingested exceeds the number consumed, there is an increase in body weight. Only when water retention occurs, an accompaniment of some serious illnesses, can the body weight increase when the energy ingestion does not exceed energy expenditure. In all other cases, *increase in body weight* indicates the ingestion of more calories than are expended. When the energy ingestion falls below the energy expenditure, there is loss of body weight. This is contrary to the claims of some individuals that "no matter what I do, I can't gain weight" or "Everything I eat, goes to fat." Careful study of the relation of diet to body weight was carried out by Newburgh. Subjects, both obese and lean, were hospitalized so that their energy expenditure could be determined with some accuracy and so

that food ingestion could be strictly supervised. In all cases loss of weight eventually occurred when the energy ingestion was lower than expenditure and rose when it was higher than expenditure. The loss of weight was not regular, sometimes reaching a plateau, but it eventually reached the amount expected.

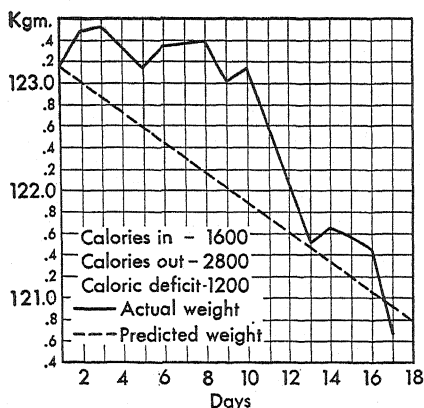
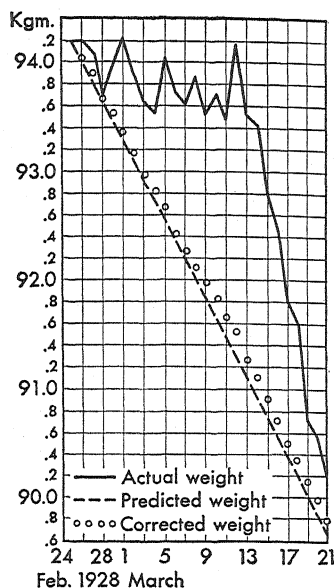


Fig. 30-3. The relation of actual weight to predicted weight loss in two patients on a low-calorie diet. Although the loss in weight is delayed for some days, it eventually is equal to the predicted loss when retained water is excreted. (Courtesy of Dr. L. H. Newburgh and *Physiological Reviews*.)



“Glandular disturbances” have also been frequently blamed for obesity. It is true that in hypothyroidism, for example, the basal metabolic rate falls, the subject does not feel like doing strenuous activity and the total energy expenditure is low. But if he gains in weight, it is because he is eating more calories than he is expending. Even with this intriguing subject, body shape, the law of conservation of matter and of energy still holds.

NEW TERMS

Oxycalorimeter, basal metabolic rate, specific dynamic action.

QUESTIONS

1. Describe a calorimeter and explain how it can be adapted to the determination of the amount of heat given off by a man.

2. How does an oxycalorimeter differ from a calorimeter? What is measured in the oxycalorimeter? How does this give the amount of heat produced?
3. What factors influence the basal metabolic rate and in what direction? Explain.
4. What must be considered in order to calculate the total energy expenditure?
5. How can you account for the fact that emotions cause the energy expenditure to rise?
6. How can you account for the fact that the energy expenditure rises whenever there is an increase in activity?
7. Describe the specific dynamic effect of food. When have you observed it?
8. What is the relation between the balance of calories ingested and calories expended and the body weight? Is this always true? Are there any exceptions?

Excretion

A healthy body must not only be supplied with nutrients for the building and maintenance of tissue and for the production of energy, but it must also get rid of the compounds which are produced in metabolism and those which are taken in but which are not used. Normal excretion from the body is as important in the maintenance of health as is proper nutrition. The organs

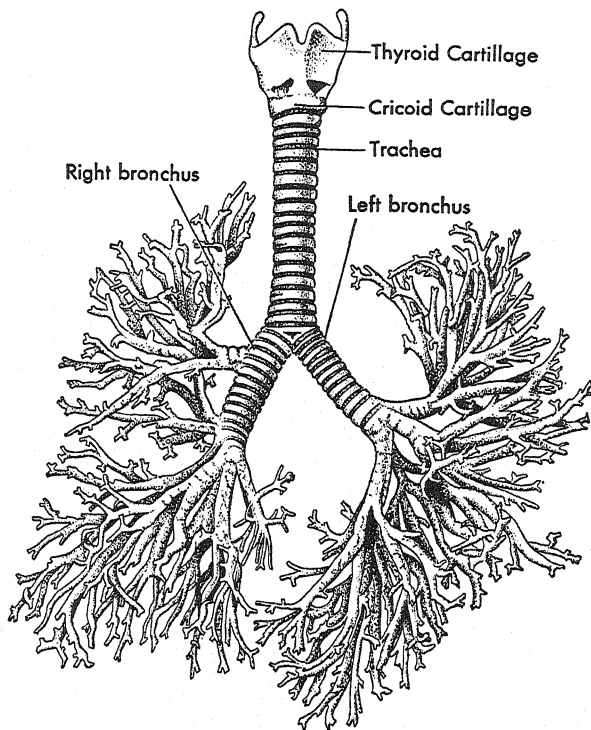


Fig. 31-1. From Greisheimer, *Physiology and Anatomy*. (Copyright by J. B. Lippincott Company.)

from which excretion takes place are: the lungs, which produce expired air; the skin, which excretes sweat; the intestines, which excrete feces; and the kidneys, which excrete urine.

EXPIRED AIR

The lungs are composed of tiny sacks called the alveoli which have a very thin membrane and a close contact with the blood through numerous capillaries which run through the lung tissue. One tiny sack is called an alveolus. These alveoli are connected to small tubes, the bronchioles, which terminate in large tubes, the bronchi. Each tube is called a bronchus. The two bronchi end in the trachea. When the movements of the chest muscles squeeze on the lungs, gases are pressed out of the alveoli, through the bronchioles, then the bronchi, the trachea, and finally the nose. During ordinary shallow breathing when you are sitting quietly, the volume of gases which is breathed out and then

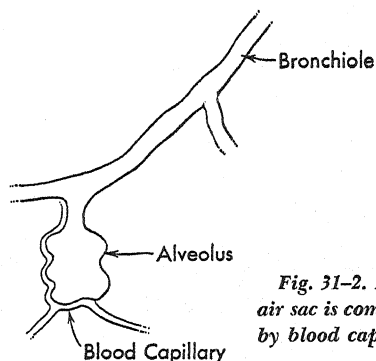


Fig. 31-2. Diagram of a respiratory unit. Each tiny air sac is composed of a number of alveoli surrounded by blood capillaries.

in is small. Of the air which is breathed in, some remains in the bronchi and bronchioles to be breathed out in the next expiration. Only part of the oxygen which is breathed in comes into the alveoli and has the chance to be absorbed into the blood through the membranes of the alveola wall and the blood capillaries. Both the inspired air and the expired air contain oxygen,

Approximate Composition of Dry Respiratory Air

	Oxygen	Carbon Dioxide	Nitrogen
Inspired air	20.96%	0.04%	79.0%
Expired air	16.0	4.4	79.6
Alveolar air	14.2	5.5	80.3

although the concentration is lower in the expired air. Carbon dioxide is rapidly lost by the blood to the alveolar air and then is driven out in the expired air. The relative amount of nitrogen in the expired air is increased because of the removal of oxygen in the alveoli.

The rate of respiration and the depth of respiration are controlled by both voluntary and involuntary processes. The involuntary movements are affected by the concentration in the blood of carbon dioxide through its influence on the respiratory center in the brain. When the concentration of carbon

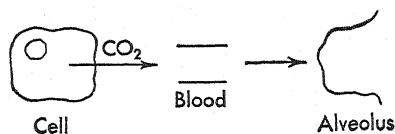


Fig. 31-3. Carbon dioxide is carried by the blood from cells to the alveoli of the lungs.

dioxide in the blood rises during exercise, the respiratory center sends out nerve stimuli which cause breathing to become more rapid and deep. This process eliminates carbon dioxide more rapidly from the alveoli and consequently allows the loss of carbon dioxide from the blood to increase. As the blood concentration of carbon dioxide falls, respiration becomes slower and more shallow.

The source of the carbon dioxide which is eliminated in respiration is the metabolism of carbon compounds in the cells. When a cell oxidizes a molecule of carbohydrate, fat, or amino acid, the carbon end product is usually carbon dioxide. Other carbon compounds which have not been studied are also oxidized in small amounts to produce carbon dioxide. This product passes through the cell wall into the blood stream and is finally excreted in the expired air.

The expired air is also a channel of excretion for water. Air in the alveoli becomes saturated with water, and when this air is breathed out, water is lost from the body. You are familiar with this fact from your observation of the cloud of condensed water droplets which you breathe out on a cold day. If the expired air is cooled quickly, the saturation point of this small puff of air is exceeded, and the water condenses as droplets. The expired air soon mixes with the outside air and the droplets evaporate and disappear.

SWEAT

Sweat is produced on your skin at all times and in all temperatures. When the amount produced is very small, as when your surroundings are cool or when the sweat evaporates very quickly in a dry atmosphere, you may not be aware that any is produced. Nevertheless, it has been demonstrated that considerable sweat — between 300 and 700 milliliters per day — is lost in this fashion. This is called *insensible perspiration*, while the sweat which forms droplets on your skin and of which you are aware, is called *sensible perspiration*. Sweat is over 99 per cent water with a small amount of sodium chloride and very small amounts of protein and urea.

Approximate Composition of Sweat *

Urea N	19-21 mg./100 ml.
NH ₃ N	4-6
Amino acid N	5-6.5
Glucose	12-20
Cl ⁻	0.15-0.37
PO ₄ ⁼	6-6.5
Organic acids	13-45 meq./100 ml.
(65-85% lactic acid)	

During the war, there were extensive studies of the composition of sweat, since many troops were stationed in tropical regions where excretion by sweating is much more extensive. It was considered a possibility that water-soluble vitamins might be lost through the sweat and that a man might, therefore, have a higher requirement for vitamins in the tropics than in the temperate zone. Careful study of many subjects indicated that the loss of vitamins in the sweat was negligible in most cases and small in others.

The loss of sodium chloride by sweating becomes a problem when an individual is exposed to intensely hot, dry air. Men who work around furnaces or on the desert sometimes suffer a deficiency of salt. This may be avoided by increasing the consumption of sodium chloride. Some factories provide salt tablets for their workers, while others add salt to the drinking water.

* Compiled from McSwinney (1934), Whitehouse (1935), and Courand (1935).

FECES

The formation of the feces and their composition have been discussed in Chapter 26. The excrement from the large intestines contains not only small amounts of foodstuffs which have escaped digestion or are incapable of digestion and residues of the digestive fluids, but also true waste products. The pigment portion of the hemoglobin molecule is excreted in the bile into the intestine and leaves the body as the colored matter of the feces. Cholesterol is another normal bile component which may be a waste product. It and its reduction products appear in the feces. Some inorganic ions, such as iron and manganese, are excreted in the bile while calcium is excreted largely by way of the intestinal wall. These ions, then, leave the body by way of the feces. The total fecal bulk includes large numbers of bacteria, living and dead, and the feces contain much material which is produced by the bacteria living in the large intestine. The feces are one of the important excretory products of the body, but they contain only small amounts of the compounds given off by the cells which make up the body tissues.

URINE

Urine is the excretion which contains most of the waste products of metabolism. Urine is formed in the two kidneys. They are firmly attached to the back of the body cavity, one on each side of the spine, and they contain a very rich blood supply. As the blood flows through the numerous blood capillaries in the kidneys, compounds are removed to form urine. This process, with the help of the other mechanisms for excretion, maintains a constant composition of the body fluids. Although the production of waste materials may vary considerably with variations in exercise and food, the excretory processes are capable of maintaining a fairly constant concentration in blood and intercellular fluid. If the process for urine formation fails, death follows soon after.

A tube runs from each kidney to the urinary bladder. These are the ureters, and urine continually drips down through them and is collected and stored in the bladder. The bladder is emptied by relaxing the muscles around the urethra, a tube which leads out of the bladder.

The process by which urine is formed is a remarkable mechanism by which blood is filtered, the filtrate is concentrated, and many compounds are returned to the blood. The study of this mechanism involved a brilliant and patient investigation of minute droplets of filtrate and a careful microanalysis of their composition. It was carried out by Richards of the University of Pennsylvania.

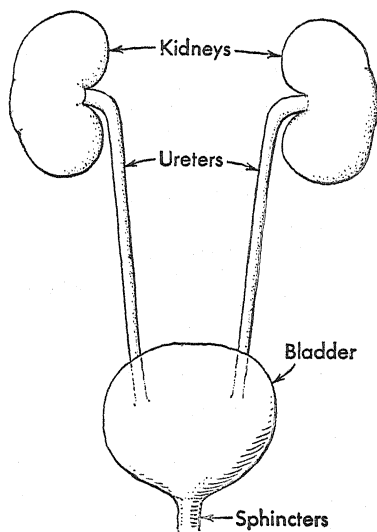


Fig. 31-4. Urine storage in the body. Urine is continually excreted by the kidneys. It flows down the ureters and is stored in the urinary bladder. The bladder is emptied and urination occurs, when the sphincter muscles are relaxed.

Urine Formation

The kidneys are made up of a very large number of small bodies, the Malpighian corpuscles, each of which consists of a capsule and a glomerulus. A tiny blood vessel runs into the capsule and there it divides into blood capillaries. These capillaries then merge and form the blood vessel which emanates from the capsule. The bundle of capillaries in the capsule is called the *glomerulus*. A tiny tubule is connected to the capsule, and fluid flows down it and is collected in the collecting tubules. This tiny tubule is also richly supplied with blood. When blood flows through a glomerulus, water and compounds dissolved in the water pass through the walls of the capillaries of the glomerulus and then through the wall of the capsule. The proteins which are colloiddally dispersed in the plasma and the blood cells do not pass through into the capsule. This process is similar to a filtration, and the fluid which collects in the capsule is called a blood filtrate. The blood filtrate flows down the tubule and

gradually changes in composition. Some substances are reabsorbed into the blood through the wall of the tubule and the walls of the capillaries which surround it. Other substances are not absorbed and, since some water leaves the fluid, they actually become more concentrated. Glucose is an example of a substance which is absorbed from the fluid as it passes through the tubule. If the concentration of glucose in the blood is 100 milligrams per 100 milliliters of blood, the concentration of glucose in the fluid of the capsule will be 100 milligrams per 100 milliliters. As the fluid passes down the tubule, the concentration of glucose falls until finally, when the fluid flows into the collecting tubule, there is little or no glucose present. The capacity of the tubule to absorb a compound is called the *renal threshold*. For most human beings, the renal threshold for glucose is between 140 and 180 milligrams per 100 milliliters, with an average at 160 milligrams per 100 milliliters. This means that 160 milligrams per 100 milliliters is the maximum concentration of glucose which can be reabsorbed in the tubule. If the blood glucose level rises above this, not all the glucose filtered out into

the fluid of the capsule will be reabsorbed and some will appear in the urine.

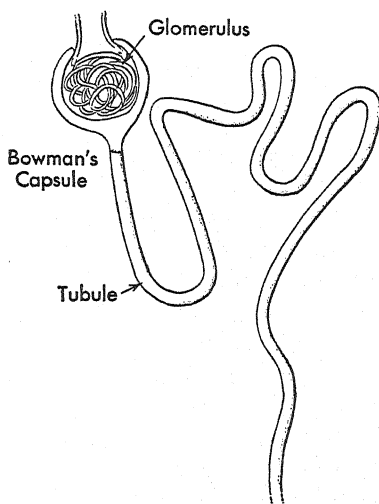


Fig. 31-5. Diagram of a unit of a kidney. When blood flows through the capillaries which comprise the glomerulus, water and dissolved substances in the blood pass through the walls of the capillaries and the Bowman's capsule. As the solution passes through the tubule, water and many other substances are reabsorbed.

Urine is formed, then, by (1) the filtration of water-soluble substances into the capsule from the glomerulus, (2) the reabsorption of water, glucose, and some other but not all other sub-

stances as the fluid flows down the tubule, and finally (3) the collection of the urine in the collecting tubules. Many of the Malpighian bodies are operating at the same time so that the urine flowing down the ureters into the urinary bladder is the result of a many-fold operation of this process.

Urine Composition

The composition of the urine varies with a number of factors, such as the size of the individual, the food and fluid ingestion, exercise, and environmental temperature, but it is normal within certain limits. The volume or the water excretion show wide variation from individual to individual and also for the same individual at different times.

Approximate Composition of Human Urine per 24 Hours

Water	0.6-1.5 liters
Urea	25-30 grams
Uric acid	0.6-1 gram
Creatinine	1.2-1.7 grams
Ammonia	0.5-1 gram
Sodium ion	3-5 grams
Potassium ion	1.5-2.5 grams
Chloride	6-10 grams
Sulfate	2-3.4 grams
Phosphate	2.5-3.5 grams
Pigments	Small amounts
Other organic compounds and ions in small amounts	

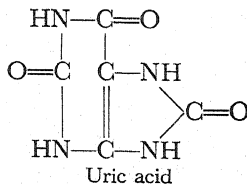
The excretion of water is influenced by the total volume of water ingested in beverages and in food, external temperature, the amount of exercise, diuretics, and hormones of the pituitary gland. Your own personal experience has taught you that as the ingestion of water increases, the amount of water excreted increases. This is a fairly rapid response, so that the water balance of the body is carefully maintained. When the loss of water in sweat is large, the urine volume decreases. In hot, dry weather even with a much increased intake of fluids, the urine volume may be considerably below 1,000 milliliters per 24 hours. During strenuous exercise, the urine volume diminishes. *Diuretics* are substances which cause an increase in the volume of urine. Several foods contain compounds which have

diuretic effects; outstanding are coffee, tea, and cocoa. Some compounds are used medically which do not occur normally in food in order to increase the flow of urine. For example, when sulfa drugs are administered and when it is desirable to maintain a large urine flow so that these drugs will not be precipitated in the kidneys, diuretics are sometimes administered. The posterior and anterior portions of the pituitary gland produce hormones which influence the volume of the urine. That from the posterior pituitary decreases the urine volume, while that from the anterior pituitary increases urine volume. They probably operate together to regulate the urinary volume and maintain a normal water balance.

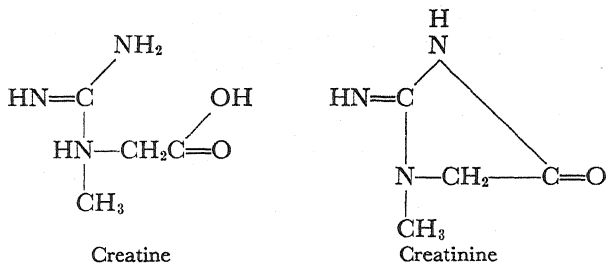
The source of the components of the urine cannot be studied in detail, but the origin of some of them will be recalled.

Urea, NH_2CONH_2 , is produced in the liver from ammonia. The source of the ammonia is in the oxidative deamination of amino acids. When the liver cells form urea, it passes through the cell walls into the blood stream and is carried to the kidneys. In the kidneys, much of the urea is excreted into the urine according to the process described above. Urea is not reabsorbed as the blood filtrate passes down the tubule. Instead, as water is reabsorbed, the concentration of urea in the fluid increases. The amount of urea excreted in urine in a 24-hour specimen reflects the level of protein catabolism. When the diet is high in protein and the amount of amino acids available for deamination is large, the urea excretion is high. On a low protein diet, the 24-hour excretion of urea is low.

Uric acid is the end product of the metabolism of purines. These are compounds which form part of the molecule in nucleic acids and, by this, in nucleoproteins. Nucleoproteins are of great importance in the nucleus of the cells, and the metabolism of these substances is likewise important. This portion of metabolism was not studied, although nucleoproteins were mentioned in the discussion of conjugated proteins.



Creatinine is the end product of creatine phosphate, one of the phosphates of muscle. When a muscle contracts, glycogen is phosphorylated and then undergoes a long series of chemical transformations. One of the compounds which supply phosphate is creatine phosphate. Some creatine phosphate is continually lost from muscles as creatinine into the blood and then into the urine. The quantity of creatinine excreted in the urine in a 24-hour period reflects muscle bulk. Men with large, well-developed muscles excrete more creatinine than women with small muscles. Exercise does not increase the excretion of creatinine, although a long period of training in which the muscles are developed will result in a gradual increase in creatinine excretion.



The source of the urinary sodium and chloride ions is in the food. Many foods contain small amounts of sodium chloride, but the bulk of that eaten is used as a condiment. If no salt is added to the food, either in cooking or serving, the excretion of sodium and of chloride immediately falls. On the other hand, if large amounts of salty food, such as potato chips, ham, or popcorn are eaten, the excretion of sodium and chloride ions immediately increases. The quantity of sodium chloride in the body is maintained at a fairly constant level by the rapid change in urine concentration with changes in the quantity eaten.

The urine, then, is one of the chief channels of excretion for many of the products of metabolism. It is not surprising that the normal functioning of the kidneys is essential to health. It is possible to excrete sufficient urine from one kidney. There are many records in medical history of individuals who have had one kidney removed and who lead normal lives. But when both kidneys fail and urine is no longer formed, death follows soon after.

NEW TERMS

Insensible and sensible perspiration, renal threshold, diuretic, glomerulus, Malpighian corpuscle.

QUESTIONS

1. Describe how expired air is excreted. How does it differ in composition from inspired air? What is the source of these compounds?
2. What important function does sweat serve? Is the loss of compounds other than water appreciable in sweat? What are they? Do we sweat in winter time?
3. What excretory products are lost to the body by way of the feces? What is their origin?
4. Describe the formation of urine.
5. What compounds and groups of compounds are excreted from the body by way of the urine? What is the source of each?

TEXTILE CHEMISTRY

Textile Fibers

Many of you have had or will have a course in textiles in which classification, weaving, characteristics, and applications of common fabrics are studied or through your interest in clothing and household furnishings you are already familiar with many aspects of the field of textile fibers. In this chapter the many types of fibers with which you come in contact will be reviewed and their chemical structure and chemical reactions and the processes for synthesizing fibers will be studied more thoroughly.

Fiber Classification

Natural Fibers

Vegetable

- Seed fibers (cotton, milkweed)

- Wood fibers

- Stem, bark of bast fibers (linen, hemp, jute, ramie)

- Leaf fibers (Manila hemp, sisal)

- Fruit fibers (coconut fiber)

Animal

- Hair and wool (sheep, rabbit, goat, llama)

- Silk

- Feathers

Mineral

- Asbestos

Synthetic Fibers

Organic fibers

- Rayons

- Nylons

- Regenerated proteins

- Resins

Inorganic

- Glass wool

- Metallic threads

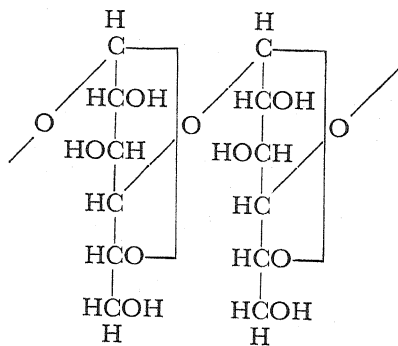
CHEMICAL COMPOSITION

Chemically fibers fall into two main groups, cellulose fibers and protein fibers. The vegetable fibers are all more or less pure cellulose while rayons are either regenerated cellulose or cellulose esters. Animal fibers on the other hand are bundles of protein molecules with other materials present in small amounts. So, too, are some of the new synthetic fibers made of casein, peanut or soybean protein. The nylons are closely related to proteins.

The resins and the inorganic fibers do not fall under this classification. However, at present they are not used extensively for either clothing or domestic goods.

Cellulose

You will remember that cellulose is a polysaccharide composed of 100 to 120 glucose units joined together by an ether link between the 1 carbon on one glucose and the 4 carbon on another.



Possibly there are a number of different cellulose molecules which differ slightly in molecular weight, much as there may be a number of starches.

The structure differs from that found in starches in (1) the number of glucose units and (2) the configuration or arrangement in space of the groups around the 1 carbon.

Textile fibers such as linen or cotton fibers are made up of *bundles* of cellulose molecules. The difference in microscopic

appearance of these fibers is probably caused by a difference in the arrangement of the bundles of molecules and possibly by a difference in the small amount of cementing substances, but not by a fundamental difference in the chemical structure of the cellulose. It is difficult to determine whether there are slight chemical differences as in the number of units of glucose in cellulose from cotton or linen.

The functional groups in cellulose are alcoholic. For each glucose unit there is one free primary alcohol group, $\text{—CH}_2\text{OH}$, and two secondary alcohol groups, —CHOH . The bonds which hold the glucose units together are ether links, —C—O—C— . Thus cellulose will react as a high molecular weight alcohol or ether.

Vegetable fibers are not composed entirely of cellulose. All contain water in amounts varying with the humidity of the atmosphere, as well as other impurities. These impurities are waxes, gums, pectic acid, and coloring matter. In raw cotton they amount to 4 to 6 per cent, while in untreated linen they are present between 15 and 30 per cent. They may be partially or almost completely removed in processing the fibers. The difficulty in wetting new unbleached muslin is caused by the presence of waxes on the cotton fibers. Bleaching removes some of these materials, but the coloring matter in particular.

ACTION OF CHEMICALS

Cotton, linen, and other vegetable fibers react similarly in the presence of acids and bases, although the percentage of impurities present may influence the *extent* of the reaction.

Acids

In general, concentrated mineral acids will destroy cellulose fibers. Cold dilute acids have slight effect if they are not allowed to dry (and hence become more concentrated) on the fabric. Hot acids are more active and are likely to make the fibers tender. Concentrated sulfuric acid causes the fiber to swell and, if it is quickly removed by washing, to become hard. This reaction is used in producing "permanent finish" or "Swiss finish" in cloth. If contact with the concentrated sulfuric acid is extended, the cellulose is hydrolyzed to dextrins and disappears by

solution. Cold concentrated nitric acid forms nitrate esters of cellulose producing the nitrocelluloses. These are used in gun powder, celluloid, collodion, as a plastic coating, and once were extensively used as rayon. The nitrocelluloses differ in the extent of nitration. Hot concentrated nitric acid causes the complete disintegration of the fibers.

Alkalis

Alkalis in general do not weaken cellulose fibers but instead strengthen them.

The process of "mercerizing" involves the use of alkali. Sodium hydroxide is the agent used to bring about mercerizing. If fabric is dipped in 22–32% NaOH, the cloth shrinks, gains in tensile strength, and dyes more readily. If yarns are dipped under tension, so that shrinkage is avoided, a silky luster develops. The sodium hydroxide must then be removed by washing.

Protein

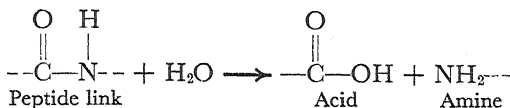
You will remember that proteins are very large molecules which yield amino acids on hydrolysis. These amino acids are held together primarily by peptide links. The proteins which constitute the major part of wool, silk, and hair are long slender molecules of the simple proteins, albuminoids. That of wool and hair is called keratin while that of silk is called fibroin.

Microscopically a wool fiber is composed of a medulla or central portion which is very small in high-grade wool, the cortex which contains many spindle-shaped cells, and a horny covering resembling scales.

In silk there is an absence of cells. The fiber is a long filament of the protein fibroin, covered by a thin layer of gummy material known as sericin or silk glue. The sericin is removed during manufacture of the raw silk into silk cloth.

Action of Acids and Alkalis

Proteins are readily hydrolyzed by both acids and alkalis to amino acids. The peptide links are sensitive to hydrolysis in the presence of either type of reagent.

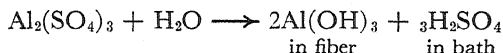


Hence it is found that protein fibers are readily destroyed by either concentrated acid or alkali, and the speed increases with increased concentration and increased temperature. Dilute acids have a much slower action and can safely be brought in contact with wool or silk fibers for short periods of time. Dilute alkali very rapidly injures the fibers.

Nitric acid, even when dilute, will produce a yellow color with protein fibers. This is the xanthoproteic reaction which is used to detect proteins. You will remember that the yellow color results from the nitration of the benzene ring which is present in the amino acids phenylalanine and tyrosine.

Metal Salts

When wool or silk is steeped in solutions of metal salts, such as aluminum, iron, and tin, the hydroxide of the metal is left on or within the fiber while the bath contains the acid.



This may be a process of both absorption into the fiber and adsorption on the fiber. The reaction is used in *mordanting* and also in weighting silk. Silk fabrics are soft and filmy, but they may be made heavier by "weighting." This is valuable for some uses since the fabric hangs and drapes better.

SYNTHETIC FIBERS

For many years man has been attempting to copy the silkworm. The silkworm secretes a gelatinous fluid which is forced through a tiny orifice, the spinneret, and which hardens into the silk filament on contact with air. As early as 1842, Schwabe reported a method of forcing a coagulable solution through small holes for the production of a filament. A number of patents were issued in Britain during the next fifty years for the production of artificial silk. It was not until the 1890's, however, that a com-

pany was actually formed and synthetic fibers were produced commercially. For almost forty years the development of synthetic fibers was slow, but steady. During the past twenty years synthetic fibers have achieved great importance. Most women possess many garments and domestic articles made partially or completely of synthetic fibers.

The term "artificial silk" was used extensively in the early decades of the development of manufactured fibers. It was an unsatisfactory designation because the fibers then produced differed markedly from silk and also because it aroused buyer resistance in implying that the product was a substitute and thereby inferior to silk.

The term "synthetic fiber" or "synthetics" is now applied to these products, but this term, too, is not completely satisfactory. Many rayons are reconstituted cellulose and in this sense are perhaps not actually synthesized. However, these are the terms now in general use.

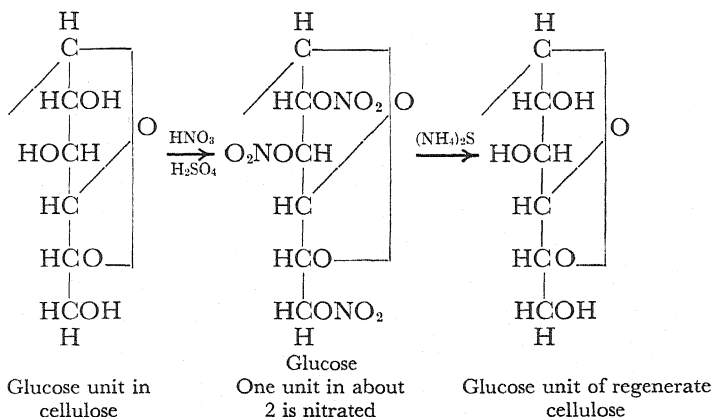
Rayons

Rayons are fabrics or fibers of either (1) regenerated cellulose or (2) cellulose esters — acetate or nitrate (Chardonnet, Tubize, collodion rayons). The United States Department of Commerce defines rayon as "The generic name of filaments made from various solutions of modified cellulose by pressing or drawing the cellulose solution through an orifice and solidifying it in the form of filament or filaments by means of some precipitating medium." In 1948 the consumption of rayons in the United States reached 913.7 million pounds compared to 487 million of wool, 3511.7 million of cotton, and 5.7 million pounds of silk.

When cellulose is treated with nitric acid or with a mixture of nitric and sulfuric acids, the free alcoholic groups of the cellulose are esterified and nitrates are produced. The extent of nitration is controlled by the nitrating medium, the length of the contact, and the temperature. Highly nitrated celluloses (13–13.3% N) are explosive and are used as guncotton. The nitrocellulose used for rayon fibers has a lower nitrogen content, and this must be removed before the fiber is suitable for ordinary use. Cellulose nitrate is highly inflammable, but by removing the nitrate groups

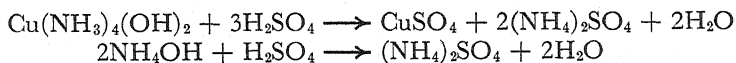
with a reducing agent such as ammonium sulfide, the inflammability is reduced to about the order of cotton.

In producing cellulose nitrate rayons, the cellulose is nitrated and dissolved in an alcohol ether mixture. It is forced through spinnerets into a warm, moist atmosphere or into warm water where the filament is precipitated. The fiber is then treated with a sulfide to reduce the nitrate groups and produce cellulose.



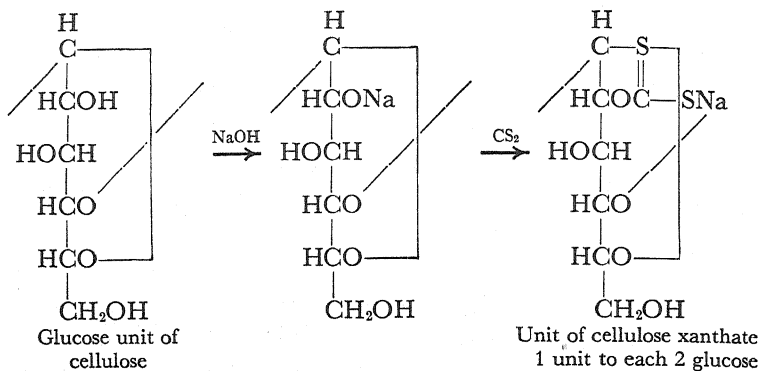
Since 1940 this process has not been used in the United States to any extent.

Cuprammonium Rayon (Bemberg) A solution of copper ammonium hydroxide, $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$, a complex and concentrated ammonium hydroxide will dissolve cellulose. In this process the cellulose is usually derived from wood — spruce, western hemlock, or southern pine. The cellulose solution is forced through spinnerets into a dilute acid solution. Here the cuprammonium solution reacts, and the cellulose precipitates.



The amount of cuprammonium rayon produced in the United States is at present small.

Viscose Rayon This method accounts for the production of over three-fourths of the rayon in the United States. Cellulose, usually from wood, is soaked in an 18% solution of sodium hydroxide. It is aged for 72 hours and is then treated with carbon disulfide to produce cellulose xanthate.



Approximately one glucose unit out of every two in the cellulose molecule (or 50 to 60 units in one molecule) undergoes the above reaction. The product, called cellulose xanthate because of its

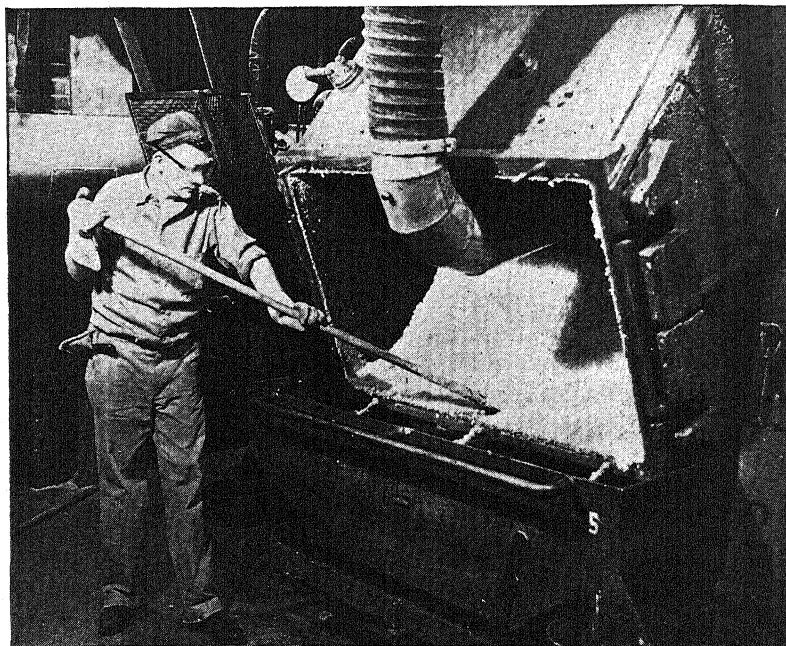


Fig. 32-1. Unloading a baratte where a batch of treated pulp has been churned and mixed with carbon bisulfide to become cellulose xanthate, a chemical step in the manufacture of viscose process rayon. The pulp emerges deep orange in color. (Courtesy of E. I. du Pont de Nemours and Company.)

yellow color, is soluble in NaOH solution. Strong acid splits off

the $\begin{array}{c} \text{S} \\ || \\ \text{—C—} \end{array} \text{SNa}$ group. The solution of cellulose xanthate in NaOH is forced through spinnerets into a bath of dilute sulfuric acid, sodium bisulfate, and glucose. The free cellulose precipitates as a filament.

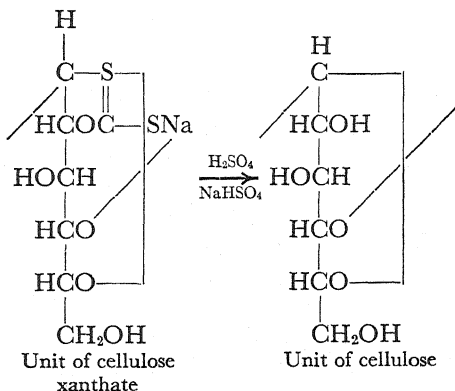
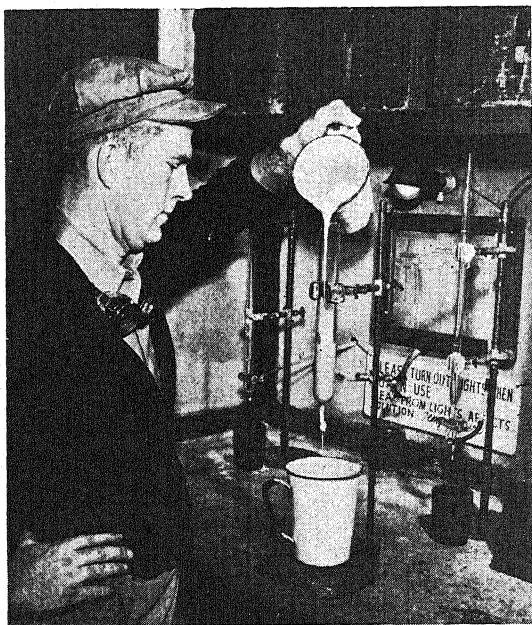
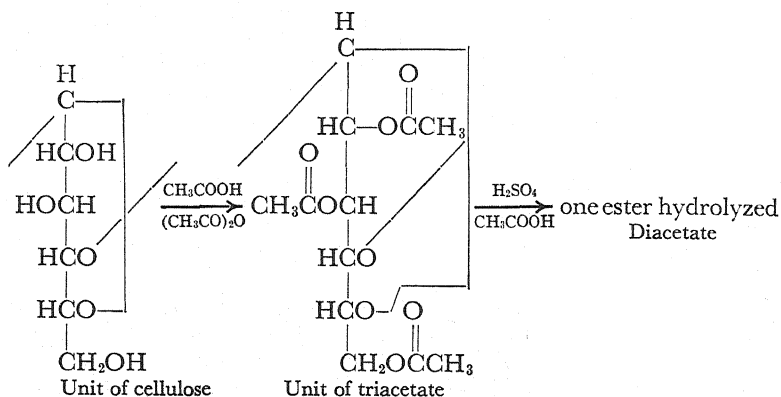


Fig. 32-2. Liquid viscose, which is "ripened" under carefully controlled temperature, is tested at regular intervals in the process of becoming rayon yarn. Here the photograph shows the liquid dripping from a tube to determine its viscosity. (Courtesy of E. I. du Pont de Nemours and Company.)



Acetate Rayon (Celanese, Chacelon, Acele, Seraceta)

Acetate rayon has steadily gained in importance during the past decade. Cotton linters, the short filaments attached to the cotton seeds, are used as the source of cellulose in this process. Cellulose is treated with a mixture of glacial acetic acid, acetic anhydride, and a catalyst to form the triacetate. This ester is not soluble in acetone and is hydrolyzed to the diacetate by a mixture of acetic acid and sulfuric acid. The diacetate is then precipitated by water as a white solid. This is dissolved in acetone and forced through spinnerets into a stream of warm air. The acetone evaporates and the diacetate is precipitated as a fine filament.



Rayon fibers are delustered by four general methods: (1) by the manner of spinning or weaving, (2) by roughening the yarn surface, (3) by depositing some foreign material on the surface of the yarn or cloth, and (4) by introducing finely divided particles such as TiO_2 into the spinning bath so that they will be occluded in the filament.

Regenerated Proteins

Casein Fiber (Aralac, Lanital) Casein, the protein of milk, is dissolved in water in the presence of alkali, and the solution is heated until it is thick and viscous and then is forced through spinnerets into a coagulating bath of formaldehyde to form filaments which can be spun.

The filaments of casein are smooth instead of scaly as wool fibers are. For this reason they do not felt. The wet fibers have

low tensile strength, but when mixed with other fibers give satisfactory fabrics. Adsorption of dye by casein filaments is slower than by wool.

Peanut Fiber Ardil is the registered trade name for a fiber made of peanut protein. The protein is dispersed in a sodium hydroxide solution and forced through spinnerets into a dilute solution of sodium sulfate and sulfuric acid. The filaments of protein precipitate and are subsequently hardened by treatment with formaldehyde and hydrochloric acid.

Soybean Fibers Soybean is an agricultural product available in a large quantity which is a good source of protein. The protein may be readily extracted from the defatted meal, dissolved, and spun much as casein. The filaments are spun and may be combined with other fibers to produce interesting and varied fabrics.

Nylon

Nylon is a generic name for synthetic fibers produced by forming a high molecular weight molecule by the condensation

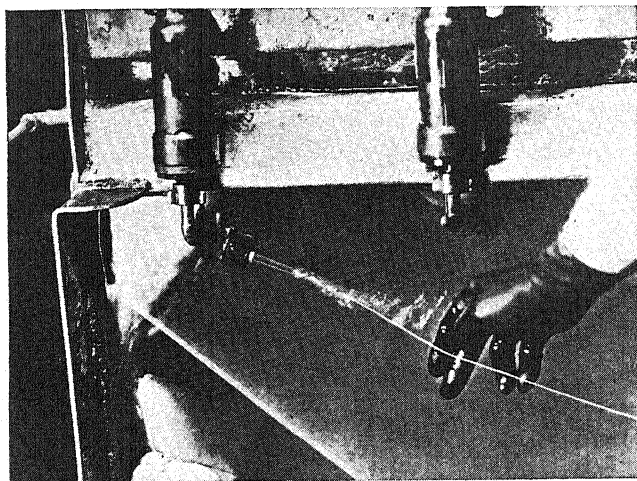
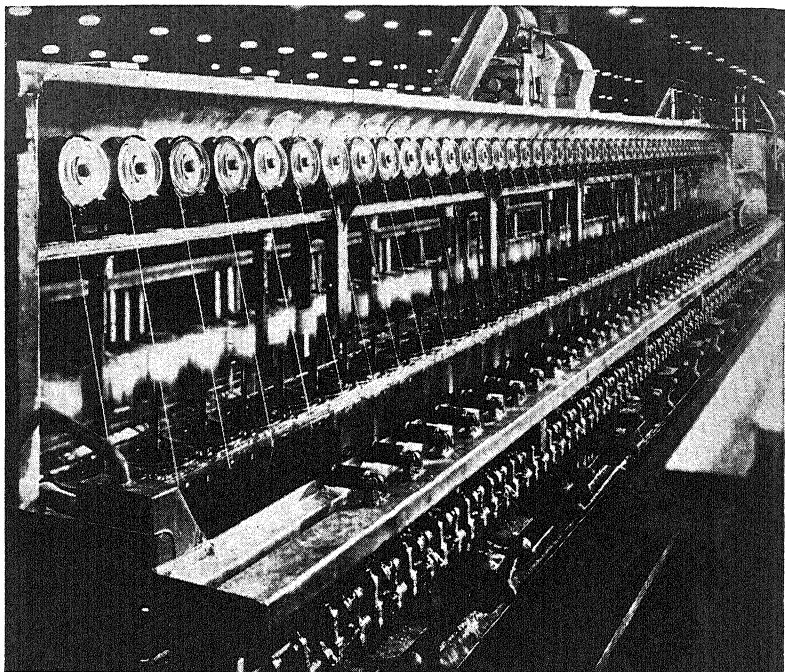


Fig. 32-3. Liquid viscose transformed in a chemical bath into cellulose filaments to make rayon thread. Note the liquid being forced through the many fine holes in the spinneret and in a short space becoming separate rayon filaments which, further on, form a rayon thread. (Courtesy of E. I. du Pont de Nemours and Company.)

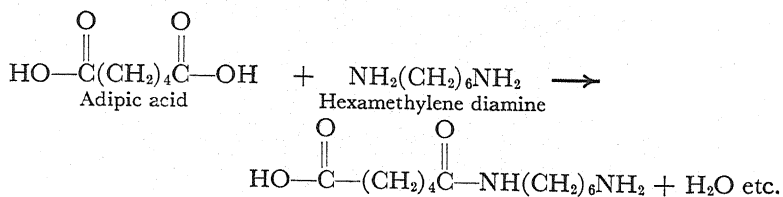


32-4. General view of a bucket spinning machine at a viscose process rayon plant. The white lines up the face of the machine are the rayon threads as they leave the chemical bath. (Courtesy of E. I. du Pont de Nemours and Company.)

of amines and acids. The patents cover a wide range of possible reactions:

1. From amino acids, imino acids, and their esters.
2. From amines with hydroxyacids; dibasic acids and dihydric alcohols; glycols.
3. From alcohols and glycols.
4. From alcohols, glycols, and aldehydes.

The nylon on the market contains nitrogen and the reaction generally given for the condensation is:



A large number of different polyamides have been produced with an average molecular weight of 12,500 corresponding to about 920 units in each chain.

The polymer is formed and then separated from the reaction mixture by precipitation with ethanol. The polymer is heated to 234° when it becomes a thick viscous fluid which is forced through spinnerets.

The fibers are readily dyed and have fine resistance to abrasion. The tensile strength of the wet fiber is high.

Vinyon

One resin fiber produced commercially at present is vinyon. Vinyon is a copolymer of vinyl chloride, $\text{CH}_2=\text{CHCl}$, and vinyl acetate, $\text{CH}_3\text{COOCH}=\text{CH}_2$. This term, copolymer, means that the two molecules react repeatedly with each other and themselves to form a long-chain molecule with a high molecular weight. The vinyon on the market is produced from 88–90% vinyl chloride and 10–12% vinyl acetate. The molecular weight is about 20,000 and the structural unit is



The copolymer is dissolved in acetone, and the solution is forced through spinnerets into



Fig. 32-5. From tiny holes in a spinneret fine filaments of nylon are extruded. All of the filaments shown here will be wound together to form nylon yarn. (Courtesy of E. I. du Pont de Nemours and Company.)



Fig. 32-6. Nylon in a variety of fabrics—marquisette, lace, foundation garment tricot, velvet, and twill. (Courtesy E. I. du Pont de Nemours and Company.)

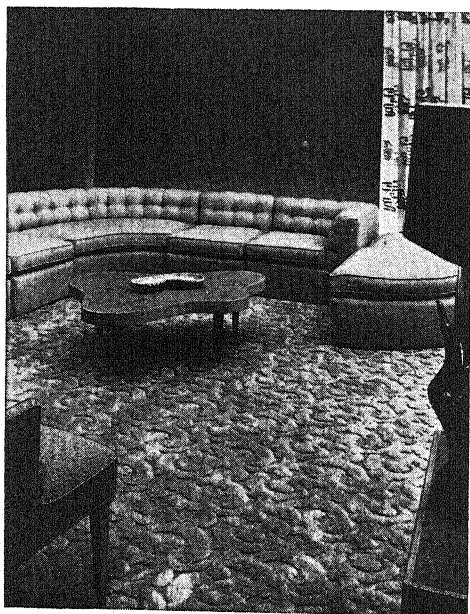


Fig. 32-7. Nylon carpeting. (Courtesy of E. I. du Pont de Nemours and Company.)

a stream of warm air. The solvent evaporates and a filament is produced. The new filament has little tensile strength, but it is slowly stretched and as the long molecules become oriented in the same direction as the filament, the tensile strength increases. The yarn is finally set under tension at 190–212° F. This stabilizes it against shrinkage up to 150° F.

Vinyon does not react with concentrated acids or bases and is not affected by mold, moths, or beetles. It does soften in hot water. It is not extensively used at present, but is in the early stages of development.

Orlon

Orlon is a polyacrylonitrile fiber, a type of resin, and is the newest synthetic fabric to enter the market. The Du Pont Company, which is producing it, claims that it is unusually resistant to sunlight and to atmospheric gases. It is not subject to stretching or to shrinking and has good tensile strength when wet or dry. It is said to have a warm hand and to drape well. It requires the same ironing temperature as nylon.

MEASURES

The *denier* (pronounced den-yay or den-yer) is a measure of the thread size. Precisely, it is the weight in grams of 9000 meters of thread. Thus if you buy a pair of hose of 50 denier, the thread is just half as thick as that in hose of 100 denier.

The *gauge* (or gage) of knitwear is the number of needles per inch or in round knit hose, per 1.5 inch. A high gauge means a fine knit. Thus 57 gauge hose is finer than 50 gauge.

The *count* in woven goods is the number of woof or warp threads per inch. This too is a measure of the fineness of the cloth. Thus 80-count percale is finer than 60-count.

QUESTIONS

1. What is the difference chemically between vegetable and animal fibers?
2. How can a protein fiber be differentiated from a cellulose fiber by the action of acids and bases? What is present in the gases given off by a burning protein fiber that is distinctly different from that

given off by cellulose fibers? What is the origin of these molecules? Explain.

3. What kind of compound is present in viscose rayon? Acetate rayon? Nylon?
4. Explain the series of reactions which are used to produce viscose rayon. Why is it sometimes called "regenerated cellulose"?
5. How can you account on the basis of structure for the difference in the properties of viscose rayon and acetate rayon?
6. What type of reaction is used to produce nylon? Does it more closely resemble protein or cellulose fibers?
7. Name some of the proteins which are being used as regenerated protein fibers. What are the possibilities in this field?

Fabric Dyeing

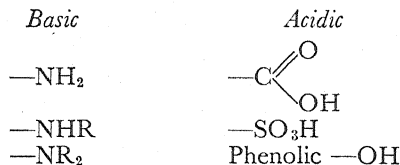
The wide variety of colors and shades which are obtainable today in fabrics are a delight to all. But when you buy fabrics you are interested not only in the color at the moment, but the fastness of that color to washing, to sunlight, and to crocking. "Crocking" is the rubbing off of a color from one fabric to another. It sometimes occurs when fabrics are in close contact as under the arms and around the waist. Colors which "bleed" on washing, or those which rub off, are a trial to any housewife. Today there is a remarkable range of colors with good fastness to washing and little tendency to crocking. However, fastness to sunlight is another thing, and few dyes are absolutely fast to sunlight.

The use of dyes in fibers is older than our oldest records. In ancient times, man learned the use of such natural dyes as indigo and Tyrian purple. Until this century the colors of fabrics were limited to a rather narrow palette. Perkin's Mauve, the first aniline dye, was discovered accidentally in 1856, but it was many years before the production of synthetic dyes was well established and began to influence the colors in fabrics.

Today most of the dyes are synthetic dyes. Almost all are organic compounds. The 1949 *Year Book of the American Association of Textile Chemists and Colorists* listed over 7600 different dyes manufactured in America. Some of these dyes are related to aniline or are derived from aniline (see Fuchsin and Malachite green below). They are often called "aniline dyes." In fact the term "aniline dyes" is sometimes loosely used to cover the whole field of synthetic organic dyes.



For an organic compound to be considered a dye it must be (1) colored and (2) have the ability to stick to some kind of fiber. A "fast" dye is one with a relatively great ability to stick to the fiber while a "fugitive dye" is one with considerable impermanence. Organic chemists have discovered that certain groups in an organic molecule yield color. These groups are called *chromophores*. Groups which aid in making the colored compound stick to a fiber and thereby dye it, are called *auxochromes*. They are acidic and basic groups such as the following:

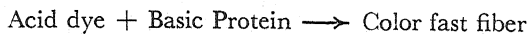


These groups have the ability to react to form salts with other acidic or basic compounds. Organic salts, in general, are water soluble and many dye salts show considerable solubility in water. This is a distinct advantage in dyeing.

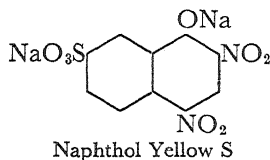
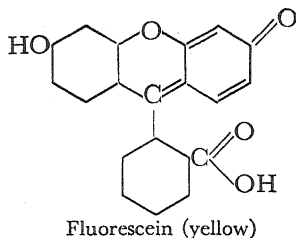
There are two theories to explain the process of dyeing, (1) the chemical and (2) the mechanical theory. Probably one applies to some dyes and the other to other dyes. The *chemical theory* assumes that a chemical reaction occurs between fiber and dye. The resultant stable compound would then be a color fast fiber. The *mechanical theory* assumes that the colored molecule becomes enmeshed in the interstices of the fiber and is thereby held fast.

Acid Dyes

These are dyes having acidic auxochromes. $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$, $-\text{SO}_3\text{H}$, or phenolic $-\text{OH}$. Acid dyes are fast and dye well on protein fibers (wool, silk, casein, etc.) but do not dye cellulose. Probably the difference in effect is caused by the presence in protein fibers of basic amino groups which react with the acidic groups of the



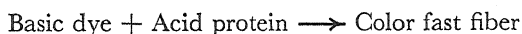
dye to form stable compounds. Examples of acid dyes are:



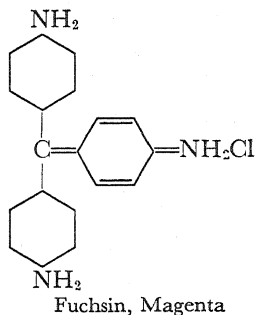
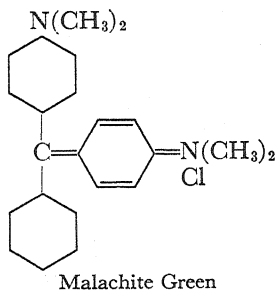
Basic Dyes

These are dyes which have basic auxochromes, $-\text{NH}_2$, $-\text{NHR}$, or $-\text{NR}_2$. Like acid dyes, they readily dye protein fibers and show good fastness. The process of dyeing, here too, probably depends upon a chemical union between the basic

groups in the dye and the acidic groups, $-\text{COOH}$, in the protein.



These dyes have little effect on cellulose fibers. Examples:

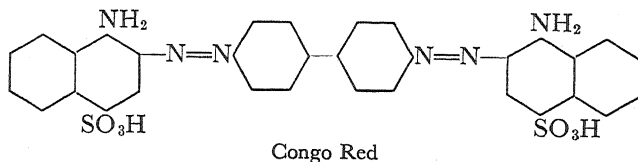


Substantive Dyes

Substantive dyes are able to dye cotton (and other cellulose fibers) directly. Many of them also dye the protein fibers.

Until fairly recent years only two dyes could be applied to cotton without the use of a mordant. They were indigo and turmeric, vat dyes. In 1884 Congo Red was synthesized and turkey red cloth and red calicos of our grandmother's day became common. This substantive dye was followed by many

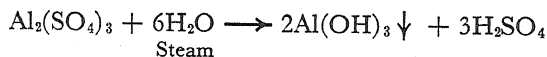
others related chemically to Congo Red. Today there are many substantive dyes of all colors.



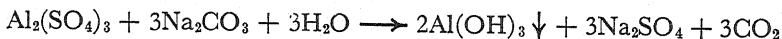
Mordant Dyes

Mordant dyes are produced by soaking the fabric in a soluble salt of acid, allowing the salt to react to form an insoluble base or acid in the fibers, and then adding an acid or basic dye which will react with the "mordant." The mordant is the acid or base deposited in the fibers, which reacts with the dye and holds it fast to the fabric. This insoluble salt formed from the mordant and dye is called a color lake.

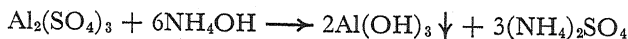
Some mordants commonly used are aluminum sulfate, potassium aluminum sulfate, ferrous sulfate, chromium acetate, tannic acid. Chemical transformation to the insoluble base is brought about by hydrolysis under the influence of steam, boiling water, or a salt like Na_2CO_3 . Occasionally NH_4OH is used.



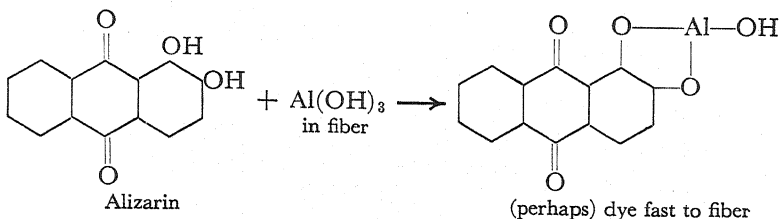
or



or



The basic $\text{Al}(\text{OH})_3$, the mordant, will then react with an acidic dye like alizarin



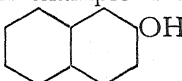
The color of the mordanted dye, the color lake, depends upon the dye used and the nature of the mordant. For example,

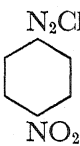
alizarin mordanted with $\text{Al}(\text{OH})_3$ produces tangerine, with $\text{Cu}(\text{OH})_2$ a grayed lavender, and with $\text{Cr}(\text{OH})_3$ plum.

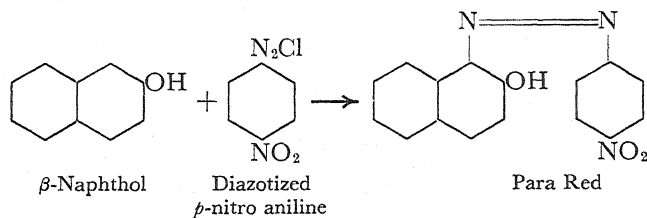
Tannic acid acts as a mordant for attaching basic dyes to fibers.

Ingrain Dyes

Ingrain dyes are dyes which are synthesized in the fiber. The fabric is dropped into one chemical, dried, and then dropped into another. The formation of the dye actually takes place in the fiber, and if it is insoluble it is trapped there and is fast to washing. An example is Para Red. The cloth is dipped in

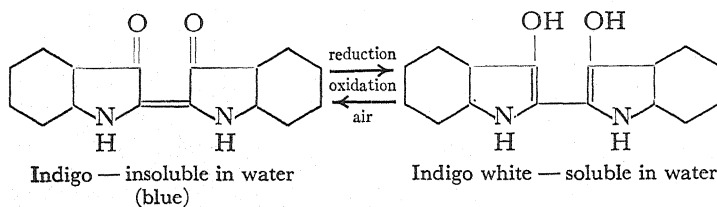
β -Naphthol , dried and then dipped into cold

diazotized *p*-nitro aniline, . These two compounds react to form the insoluble dye, Para Red.



Vat Dyes

Vat dyes are insoluble dyes which can readily be reduced to a soluble substance. The reduced dye can be colored or colorless. The fabric is dipped in the reduced dye and exposed to air. The oxygen of the air oxidizes the reduced dye back to the original insoluble dye. Indigo is an example of this:



A common reducing agent in the dye bath is sodium hyposulfite, $\text{Na}_2\text{S}_2\text{O}_4$. Since this alkaline salt is injurious to protein fibers, the method is not commonly used with wool or silk. It has been widely used for cotton goods for many years. The blue of "work" clothes, fast to an indefinite number of washings, is indigo, applied as a vat dye.

The dye bath usually contains some salt. The function of the salt is to produce a deeper color. Most dyes are colloiddally dispersed, and the presence of electrolytes cause precipitation of these colloidal particles. The quantity of salt must be regulated since a large amount will precipitate the dye too rapidly from the dye bath and prevent dyeing. Salts used are sodium chloride, NaCl , sodium potassium tartrate, $\text{NaKC}_4\text{H}_4\text{O}_6$, and sodium sulfate, Na_2SO_4 .

In washing fabrics with bleeding dyes, salt is frequently added to the rinse water to minimize the loss of color.

NEW TERMS

Crocking, bleeding, color fast, aniline dye, acid dye, basic dye, substantive dye, vat dye, mordant, ingrain dye.

QUESTIONS

1. Give two theories to explain the fastness of some dyes to washing.
2. What types of fibers will dye to a fast color with acid dyes? Why? With basic dyes? Why?
3. Why is color fastness more difficult to achieve in cotton than in wool?
4. What is a mordant? What is its function? What influence does the mordant have on the color produced by the dye?
5. What is the function of salt in a dye bath? Why are you sometimes advised to use salt in the rinse water for articles with fugitive colors?
6. Why are vat dyes fast to washing?
7. What is the advantage of an ingrain dye?
8. What kind of mordant can be used with a basic dye?

Laundering and Cleaning Textiles

Today the number of aids to laundering fabrics is so great that most housewives are confused and there is a good deal of talk about how well or how poorly these products perform. During World War II in the face of a soap shortage a number of synthetic detergents were introduced and the industry expanded enormously. Some of the products, old and new, available for cleaning textiles will be considered. The influence of hard water on cleaning with soap was discussed in Chapter 11 and of soap products in Chapter 21.

A *detergent* is a substance which has the ability to remove soil. The term is applied not only to agents which remove soil from clothing and domestic fabrics, but to substances which clean anything from steel girders and sheet metal to electric insulators. An attempt to cover the field of detergents will not be made but only those which are used for fabrics will be studied.

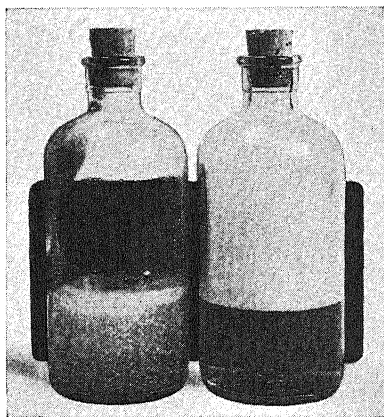


Fig. 34-1. Soap and a synthetic detergent compared in hard water. Much of the soap (left) forms insoluble calcium soaps, while the detergent (right) lathers and does not form a precipitate. (Courtesy of The Atlantic Refining Company.)

The soil which is present on most clothing is a mixture of lipides (fats, free fatty acids, phospholipides, and some cholesterol), which coat and hold fast particles of dust, cinders, carbon, etc. Almost all soil is moderately acid from the free fatty acid and perhaps other acids. If the lipide material can be removed, the particles will drop away from the fabric. In the cleaning process the redeposition of these particles on the fabric and in the fibers must be avoided. If it occurs the cloth becomes a dingy gray, the "tattletale gray" of the soap advertisements. The dirt must remain emulsified in the wash water. There is also a problem in laundering clothes of removing soluble substances, but this is much easier to accomplish than the removal of water-insoluble substances like the lipides. An effective detergent is one which removes soil and keeps it emulsified in the wash water during the laundering. In order for a soap or synthetic detergent to be efficient in removing soil, it is necessary that it must enhance the power of water to wet both the fabric and the sticky soil. This is difficult. You know how water forms droplets and runs off a greasy surface. The water must be

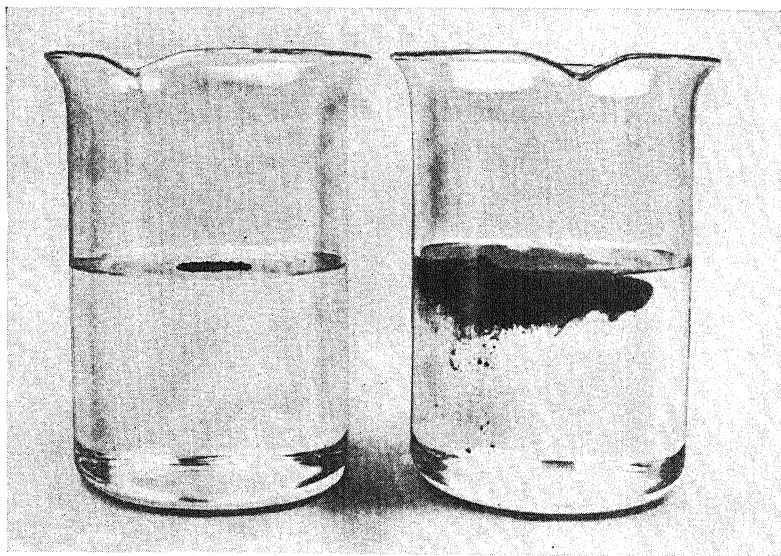


Fig. 34-2. Dispersion of soil by a detergent. Graphite is floating on water in the beaker at the left, while it is dispersed in water which contains a detergent. (Courtesy of The Atlantic Refining Company.)

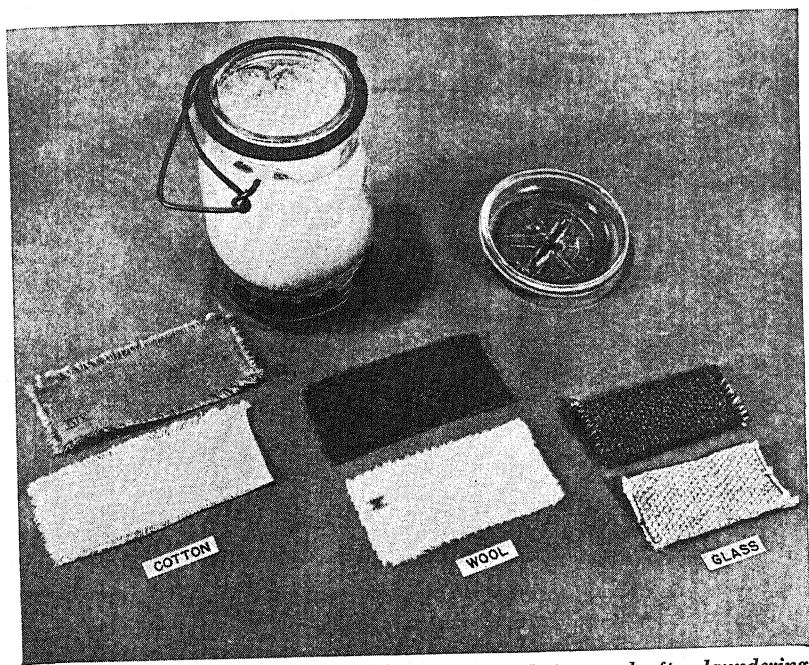


Fig. 34-3. Standard laundry tests. The swatches before and after laundering in a launderometer. The jar is the standard unit in this test. (Courtesy of The Atlantic Refining Company.)

enabled to penetrate the fibers, so that the soil particles will be lifted up and washed away. Secondly the detergent must encourage the dispersion of the soil and discourage coagulation of the particles. In other words, it must be a good emulsifying agent. The lathering power is not a measure of its efficiency as a cleaning agent. Some products which are excellent detergents produce little foam. When you are accustomed to soap, you expect a direct correlation between *amount* of lather and efficiency. Many housewives have not accepted some of the new synthetic detergents, not because they are poor detergents, but simply because they do not produce copious suds.

The efficiency of or effectiveness of detergents is compared in standardized laundering tests. Swatches of goods are uniformly soiled with a standard soil. An example of a standard soil is one composed of carbon black, free fatty acid, and fat. The

swatches are then laundered under standard conditions. For example, they may be washed for ten minutes in the same washer with water at 150° F. The detergents to be tested are added at known concentrations. The swatches are removed at the end of each test, and then all swatches are compared for their whiteness. Those with the lightest color have been washed in the presence of the most effective detergent. Sometimes the amount of carbon washed out into the wash water is also determined.

Soaps are, of course, the most widely used detergents. You will remember that they are the alkaline salts of fatty acids. Almost all the soap on the market today is a mixture of the sodium salts of fatty acids, sodium stearate ($C_{17}H_{35}COONa$), sodium palmitate ($C_{15}H_{31}COONa$), etc. Some liquid soap made from the potassium soaps is available and some soaps made from lithium salt for use in salt water.

The pH of both toilet and laundry soaps is about 10.0 to 10.3 at a concentration of 0.5%. This alkaline pH is caused by a hydrolysis of the soap which is, of course, a mixture of salts

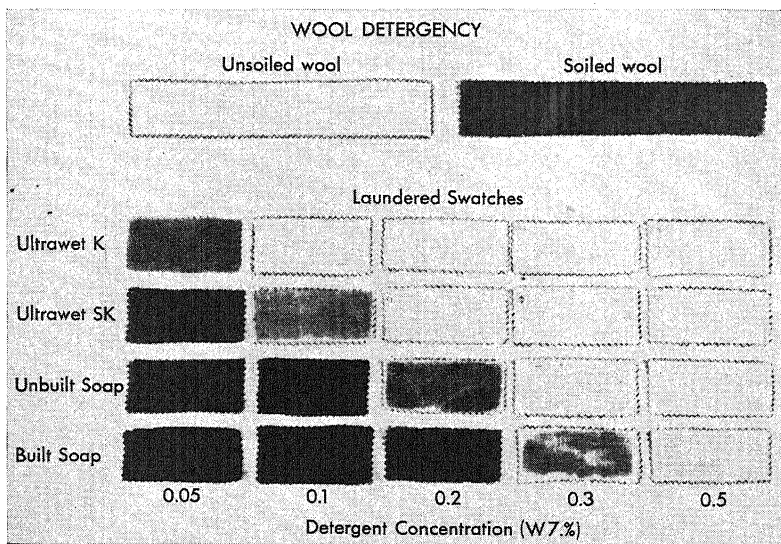


Fig. 34-4. Results of a standard laundering test with wool swatches to test the effectiveness of two detergents compared to soap and built soap. (Courtesy of The Atlantic Refining Company.)

of a strong base and weak acids. (See Hydrolysis of Salts, p. 236.) Residual sodium hydroxide would also raise the pH , but most commercial soap has little free sodium hydroxide. Homemade soap usually has considerable free sodium hydroxide.

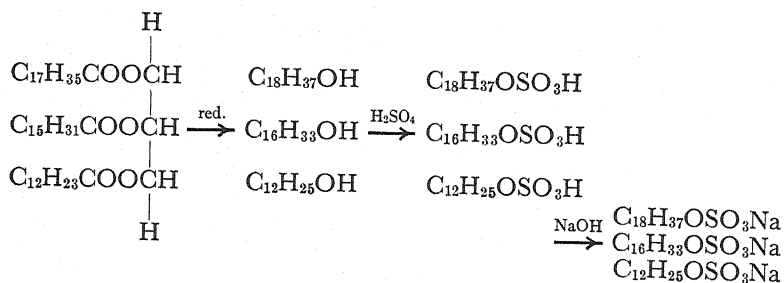
"Builders" are frequently added to soap in commercial laundries, but are not widely used in the home. They are compounds which increase the efficiency of a soap. They are alkali salts, usually sodium, of weak acids and all produce a high pH . The "building," however, is not a direct function of the pH . The most efficient are the sodium silicates (Na_2SiO_3), (Na_4SiO_4), etc., but sodium carbonate (Na_2CO_3), sodium phosphate (Na_3PO_4), and sodium borate ($Na_2B_4O_7$) are also used. The washing powders which are sometimes used in the home, particularly where water is hard, and the calcium and magnesium ions must be precipitated, act as mild builders.

Soap is an effective detergent because it has the ability (1) to emulsify lipides, (2) to absorb dirt, and (3) to wet fibers. You will remember that soap is a hydrophilic colloid and a good emulsifying agent. When a greasy fabric is churned with soap, the fatty material, insoluble in water, is emulsified into the wash water. Hot water is more efficient than cold because the greasy material is then a liquid and because most soaps are more readily dispersed in hot water than in cold. Soap also acts as a wetting agent, making water cling more closely to the textile fibers. In soft water, soaps are efficient detergents. In hard water they are very poor and the gummy precipitate which clings to the fabrics is particularly objectionable. (See Hard Water, p. 154.) Until very recently, soap in distilled water was the unsurpassed detergent for laundering cotton and lifting away the soil.

SYNTHETIC DETERGENTS

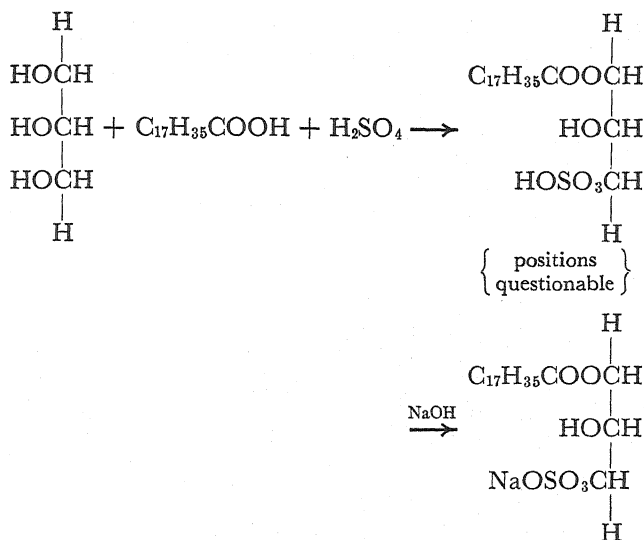
The term "synthetic detergents" is used to designate all the detergents now available other than soap. Actually soap is a "synthetic detergent" also, but it is not commonly classed with these specialized agents. ["Synthetic detergents and surface active agents," C. T. Snell, *J. Chem. Ed.* 24505-24511 (1947).]

The first synthetic detergent, which appeared over fifteen years ago, is a sodium alkyl sulfate with the general formula, ROSO_3Na . These substances are closely related to soaps since the $-\text{COONa}$ group of the soap is here replaced with a $-\text{OSO}_3\text{Na}$ in order that the detergent will not form an insoluble precipitate in the presence of calcium and magnesium ions. They are produced by catalytic reduction of vegetable oils. This yields alcohols which are then esterified with sulfuric acid. The excess acid and the ester are neutralized with sodium hydroxide.



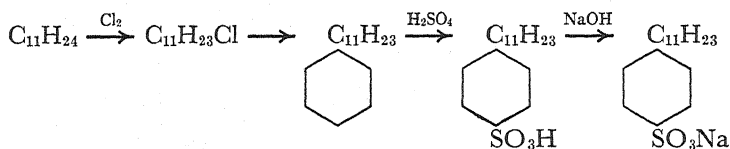
The sodium sulfate formed by the neutralization of the excess sulfuric acid with sodium hydroxide is packaged with the detergent. Extra sodium sulfate may be added to cut the product sometimes as low as one-fourth detergent. The reason for this is twofold: (1) the cut detergent is as efficient as the pure detergent and the cost of the cut product is considerably below the cost of the detergent; (2) sodium sulfate acts as a builder for these and other synthetic detergents. These detergents are excellent and inexpensive hard water detergents. They are readily dispersed in hot or cold water. They are not very stable in strongly acid solutions but in domestic laundering this is not a problem. Examples: Drene, Dreet, Duponols, Gardinols.

Closely related to the sodium alkyl sulfates are the sodium acyl glyceryl sulfates. Their properties are also very similar to those of the sodium alkyl sulfates — strong emulsification, good lathering, and fine hard water detergency. They are synthesized by the reaction of glycerol, a fatty acid and sulfuric acid to form a mixed diester. These esters and the excess sulfuric acid present are then neutralized with sodium hydroxide.



Commercial products available to the housewife of this type are Vel, Halo.

Sodium alkyl aryl sulfonates are the most important synthetic detergents in volume. They are prepared by chlorinating kerosene to form a mixture of chlorides with a chain length between C_{11} and C_{14} , and allowing these compounds to react with benzene to form alkyl benzenes. These compounds are then sulfonated with concentrated sulfuric acid and finally neutralized with sodium hydroxide.

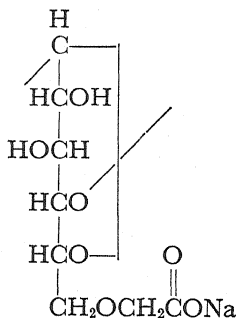


The commercial products usually contain 40 to 60 per cent active agent, while the remainder is sodium sulfate. They are very effective hard water agents and are particularly good for washing woolens. Examples are Oronite, Swerl, Ethyl Cleaner.

There are a number of other types of detergents, most of which like the above substances and soap, are termed "anionic" because they ionize to form a positive sodium ion and a negative ion (anion) of the organic radical. "Cationic" detergents such

as quarternary ammonium salts $(NR_4)Cl$ are too expensive to be used for general cleaning problems. They have not appeared on the grocery shelves. Nonionic detergents in which no ionization takes place are available on the market and represent very divergent types of substances. The product representative of this type which is available to housewives is Glim, used extensively for dish washing. It is described by its manufacturers as an alkylphenyl polyglycol ether.

Recently it has been demonstrated that Carbose acts as a promoter for arylalkyl sulfonates. It is a sodium carboxymethyl cellulose, a derivative of cellulose in which the carboxymethyl ether is probably formed on the primary alcohol of each glucose residue.



The detergency of mixtures of the synthetic detergent Carbose and alkaline salts is said to surpass sodium soaps in laundering cotton. Until this special promoter was discovered, no synthetic detergent was the equal of soap in hot distilled water for washing heavily soiled cottons. The synthetics are able to clean other types of fabrics as well or better than soap in distilled water and certainly better than soap in hard water.

Synthetic detergents are not capable of doing all household cleaning jobs with equal efficiency. "Light-weight" detergents are ones with a pH close to 7 which are particularly useful in washing silk, nylon, and wool with little loss of quality in the fabric. "Heavy-weight" detergents which contain alkaline builders produce a higher pH and are particularly useful in laundering heavily soiled cottons. Unfortunately the advertising at present makes it difficult to determine which is which. The advertisements would have you believe, of course, that this particular one is best for every household job.

All these detergents are particularly valuable in areas where the water is hard, as well as in laundering protein fibers of wool and silk which are so sensitive to high pH. A great deal of research is being directed to the understanding of the activity of these detergents and at efforts to produce better ones. You can expect an increase in the number of products available on the market.



Fig. 34-5. Washable woolens. Woolens may be treated to prevent shrinking and make laundering of woolens easy. (Courtesy of Monsanto Chemical Company.)

Synthetic Detergents

Type	Trade Name	pH of a .5% solution in soft water	Na_2SO_4	Builder
Cationic detergents				
Sodium alkyl sulfate ROSO_3Na	Dreft	7.2-7.3	?	?
	Drene	7.2-7.3	?	?
Sodium acyl glyceryl sulfates	Tide	9.8-9.9	10%	Polyphosphate
	Vel	6.9-7.2	?	?
Sodium alkyl aryl sulfonates	Halo		?	?
	Ethyl Cleaner		?	?
	Fab	9.4-9.6	30%	Alkaline builder
	Trend		70%	Small amount
	Surf	8.5-9	< 1%	?
	Swerl		?	?
	Oronite		?	?
Nonionic detergents				
Alkyl phenyl polyglycol ether	Glim		?	?
Poly ethoxy esters of fatty acids	All	7.0-8.0	None	Na_3PO_4

DRY CLEANING

In dry cleaning fabrics, solvents are used which will dissolve fat and other lipid material. The dirt then falls away from the fabric. Water-soluble substances are usually not soluble in these solvents and are therefore not removed from the fabric. They are removed by "spotting" with steam or occasionally with water. If the soiling of the fabric by water-soluble substances is great, then the garment may need to be washed in water.

The solvent most commonly used is naphtha gas. This is a rather low-boiling fraction (130–150° C.) obtained in the distillation of petroleum. It is a mixture of paraffin hydrocarbons with small amounts of impurities, whose nature depends on the source of the petroleum. These impurities are ordinarily removed before the solvent is used as a dry cleaning agent. If they are not removed, they deposit on the fabric and leave a disagreeable odor. The chief disadvantage of naphtha is its high inflammability and the relatively wide range over which it forms an explosive mixture with air. Naphtha cannot be used with safety unless stringent precautions for thorough ventilation of the room and avoidance of ignition are observed.

Carbon tetrachloride (CCl_4) is less widely used for dry cleaning, even though it presents no fire hazard. It is almost non-inflammable, so much so that it is used in fire extinguishers for chemical fires. It, too, readily dissolves lipides and allows the dirt to fall away from the fabric. It is widely used as a spot remover. In the home, spot removing is usually done while garments are being pressed. It is essential that a noninflammable fluid be used near a hot iron. Carbon tetrachloride has the disadvantage of dissolving cellulose acetate to a slight extent and of removing some dyes.

In dry cleaning establishments, detergents suitable for use with naphtha are added to the cleaning tank. They hasten cleaning and prevent the redeposition of soil on the garment. These detergents (some dry cleaners call them "soaps," but they are quite different) are not generally available for home use.

NEW TERMS

Detergent, soap builder, synthetic detergent, light-weight detergent, heavy-weight detergent.

QUESTIONS

1. How does a detergent act to remove dirt from fabrics in water?
2. What are the advantages of soap as a detergent? What are the disadvantages?
3. What is a soap builder? What type of commercially available soaps contain builders?
4. What is a synthetic detergent? What are their advantages? Do they all have the same properties?
5. Is a detergent which is excellent for washing dishes likely to be excellent for laundering? Why?
6. What is the most difficult thing to control in laundering woolsens? What detergent would you chose for this task? Why?
7. How does it happen that many synthetic detergents contain sodium sulfate? What are the functions of the sodium sulfate?
8. What is a dry cleaning agent? What are the disadvantages of naphtha gas? What are the advantages and disadvantages of carbon tetrachloride?

ABSOLUTE HUMIDITY AND WATER VAPOR PRESSURE

<i>Temperature (C)</i>	<i>Grams vapor per cubic meter</i>	<i>Tension (pressure) in millimeters of mercury</i>
6	7.3	7.0
10	9.4	9.2
15	12.9	12.8
16	13.6	13.6
17	14.5	14.5
18	15.4	15.5
19	16.3	16.5
20	17.2	17.5
21	18.2	18.6
22	19.4	19.8
23	20.6	21.1
24	21.8	22.4
25	23.1	23.8
26	24.3	25.2
27	25.7	26.7
28	27.2	28.3
29	28.7	30.0
30	30.3	31.8
31	32.0	33.7
32	33.8	35.7

ELECTROMOTIVE SERIES

1. Caesium	10. Manganese	19. Antimony
2. Rubidium	11. Zinc	20. Bismuth
3. Potassium	12. Chromium	21. Arsenic
4. Sodium	13. Iron	22. Copper
5. Barium	14. Cobalt	23. Mercury
6. Strontium	15. Nickel	24. Silver
7. Calcium	16. Tin	25. Platinum
8. Magnesium	17. Lead	26. Gold
9. Aluminum	18. Hydrogen	

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